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TO

THE JOINT SERVICES TECHNICAL ADVISORY COMMITTEE

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COLUMBIA RADIATION LABORATORY, NEW YORK, NEW YORK 10027
DEPARTMENTS OF PHYSICS, CHEMISTRY, ELECTRICAL ENGINEERING,
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December 31, 1988

COLUMBIA RADIATION LABORATORY

RESEARCH INVESTIGATION DIRECTED TOWARD EXTENDING THE USEFUL RANGE OF THE ELECTROMAGNETIC SPECTRUM

Progress Report No. 38

October 1, 1987 - September 30, 1988

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Object of the Research:

Basic research in the fields of quantum electronics; electromagnetic propagation, detection and sensing; and solid state electronics.

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FIELD	GROUP	SUB-GROUP

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dimethylcadmium; organometallic; dimethylzinc; photocathode; laser-surface interaction; photochemical deposition

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Silent light (also known as photon-number-squeezed light and sub-Poisson light) can be generated as recombination radiation from semiconductor materials by using a specially designed space-charge-limited light-emitting structure. Because such light has a photon-number distribution that is narrower than the Poisson distribution, the well-known lightwave-communication "quantum limit" of 10 photons/bit (for on-off keying) can be improved upon. We have established relationships between the bit error rate P_e and the mean number of photons per bit <N>, and between <N> and the variance-to-mean ratio of the photon number (F), for

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silent light
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bit error rate
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Diode laser
Infrared
Collisions
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Chemical dynamics
High Energy Collisions
Cl atoms
Carbon dioxide
Iodine
Doppler profile
Translational recoil
Photodissociation
Differential Cross section
Polarized
$I_2(D)$
Long range forces
Dipole-dipole mechanism
D_2S
H_2S
bistability
attosecond
femtosecond
four-wave mixing
gallium arsenide
photon echoes
sodium vapor
time-delayed four-wave mixing
Shottky Barrier
Ultrathin interface metal
Diamond Anvil Cell
High Pressure
Photoluminescence
II-VI Semiconductor
ZnSe

ABSTRACTS (Block 19 continued)

binomial-distributed silent light. <N> drops rapidly as F decreases, indicating that improved performance may be expected if silent light is used. We have also extended the open-loop fully quantum theory of light detection to include closed-loop operation. It turns out that the unmistakable signatures of nonclassical light associated with open-loop detection, such as sub-Poisson photocounts, do not carry over to closed-loop systems. Such systems can, in general, be useful for generating silent light when photon pairs are available, such as in parametric downconversion.

Transmission, luminescence and photoinduced absorption modulation techniques have been used to investigate the energy level structure of CdS_xSe_{1-x} semiconductor microcrystallites in a glass matrix. Modulation data resolves the A and B excitonic band gaps as well as a direct phonon cooperative process yielding the longitudinal optical phonon energy in the system. The band gap is blue shifted compared to the bulk semiconductor band gap. This energy shift may be attributed to confinement effects in these systems.

Broad band, incoherent, time-delayed four-wave mixing (TDFWM) has been employed to study excitation phase relaxation in dye molecules in solution and in semiconductor microcrystallites doped in glass. For excitations above the band gap, near the band edge, the semiconductor-doped glass system is homogeneously broadened with a transverse relaxation time of approximately 40 fsec at room temperature. Experiments with various optical density samples indicate, however, that for lower energy excitations, this system is inhomogeneously broadened. The transition from the homogeneous to the inhomogeneous regime is a gradual function of the optical density and the excitation wavelength. Phase relaxation of transitions between the vibrational levels of Nile Blue organic dye molecules in ethanol and methanol solutions was also investigated. At room temperature, using autocorrelation times as short as 14 fsec, no evidence of coherent transients was observed. This indicates that the transverse relaxation time is less than a few fsec. At 4.5 K, we have observed a system response indicating that the system is inhomogeneously broadened with a T_2 of approximately 7 to 10 fsec.

Work using coherent light has concentrated on studying the beats that arise when time-delayed four-wave mixing (TDFWM) experiments are done on two transitions simultaneously. Working in sodium, the effects of petahertz superposition-state modulations in the integrated TDFWM signal as a function of the time delay have been observed. As the time delay is varied, the lowest-order mixing signal modulates with a period of 980 as (attoseconds) — corresponding to the sum frequency of the two Na D lines. Higher-diffraction-order mixing signals contain modulation components at integral multiples of the doublet sum frequency; these have the effect of narrowing the peaks in the modulation pattern. Similar narrowing is expected in the lowest diffraction order for intense excitation fields.

Fermi level movements at Pt/GaAs and Ti/GaAs interfaces have been investigated using a direct measurement of Schottky barrier heights in a bimetal Schottky structure. Using thin interfacial layers, the Schottky barrier was smoothly varied from the characteristic value of the thick metal to that of the interfacial metal. The variation of barrier height vs. the inner metal thickness was found to exhibit an exponential behavior extending over a few monolayers of coverage. This experiment indicates a new approach to the fundamental study of metal-semiconductor interfaces and could be useful in device applications.

The initial stages of the optical study of II-VI semiconductor epilayers and superlattices under high pressure has been developed. Photoluminescence spectra of ZnSe layers on a GaAs substrate have been obtained down to T=10K. The pressure shift of ruby fluorescence in a diamond anvil cell has also been examined at low temperature; such ruby spectra will be used for pressure calibration.

A UV laser beam has been used to perform the first scanning photoelectron microscopy of a semiconductor surface. Using this technique, the regions of different doping levels on a semiconductor wafer were mapped. The spatial resolution was found to be limited only by the laser beam spot size.

Charged particle emission from excimer-irradiated semiconductor surfaces was studied. The emission of photoelectrons was accompanied by the emission of positive ions above a certain laser fluence threshold. A resultant

decrease of electron space charge and increase in photocurrent were observed, suggesting the use of ion emission as a source for a high current, free-electron laser, photoelectric injector.

An infrared spectroscopic technique employing the principle of total internal reflection has been used to examine the UV-induced surface photochemistry of dimethylcadmium on chemically altered silicon surfaces. Fourier transformed infrared spectra were recorded on oxidized and hydrogen "passivated" silicon surfaces (SiO_2 and SiH respectively). By monitoring changes in the infrared spectrum of adsorbed dimethylcadmium during illumination with excimer laser radiation, insight into the role of the surface in the photodissociation of the adspecies has been obtained.

A highly efficient energy exchange process has been discovered in which electronically excited I_2(D) molecules vibrationally excite a number of small molecules. The potential for achieving inverted populations in both the donor and acceptor species exists. This would lead to ultraviolet lasing in the I_2 donor and infrared lasing in the acceptor. I_2(D), which can be excited by 193 nm excimer laser radiation, is a remarkably convenient high energy species that should be useful as an initiator or catalyst in gas-gas and gas-surface chemical reactions.

Chemical reactions between chlorine atoms and a variety of H or D atom containing species have been studied using super high resolution infrared diode laser probe techniques. Rates for these reactions as well as quantum state population distributions have been measured. The magnitude of the v=1/v=0 population inversion in DCl, produced by the reaction of Cl with D_2S, has been determined for the first time.

High energy collisions between H atoms and CO_2 have been investigated. In these experiments the final vibrational state of the CO_2 produced by collisions is the bend-stretch combination level 01^11 which (unlike most CO_2 vibrational states) has both odd and even rotational levels. A marked alternation is observed in the probability of excitation of odd versus even rotational states. The recoil velocity for CO_2 in odd and even J's is quite different as well, and is related to the impact parameters which are of importance in producing a given quantum state.

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J. A. O'Neill, "Copper Etching in a Chlorine Atmosphere," Materials Research Society, Fall Meeting, Boston, MA, 1987. (contributed)

T. Cacouris, "Laser Direct Writing of Al Conductors," Materials Research Society, Fall Meeting, Boston, MA, 1987.

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J. Chou, "Rotationally Resolved Hot Atom Collisional Excitation of $CO_2(10^00)$ by Time-dependent Diode Laser Spectroscopy," Chemistry Department, Columbia University, April 20, 1988.

Lei Zhu, "The Deactivation of O('D) by CO_2," Chemistry Department, Columbia University, October 20, 1988.

COLUMBIA RESONANCE SEMINARS

"Surface Recombination via Gapstates at Semiconductor Surfaces and Interfaces," Jeffrey Bckor, AT&T Bell Laboratories, October 7, 1987.

"Dynamics of Gas-Solid Interactions," Robert Merrill, Cornell University, October 21, 1987.

"Optics of Two-Dimensional Semiconductor Electron Systems," Aron Pinczuk, AT&T Bell Laboratories, November 4, 1987.

"Optical Forces on Atoms," Harold Metcalf, SUNY Stonybrook, November 5, 1987.

"Nonlinear Optics in the Far Infrared Using Femtosecond Pulses," Dave Auston, Columbia University, November 13, 1987.

"Femtosecond Photon Echoes," Chuck Shank, AT&T Bell Laboratories, December 4, 1987.

"Open Questions in Closed-Loop Photodetection," Jeffrey Shapiro, MIT Lincoln Laboratories, December 9, 1987.

"Some Thoughts on Squeezing," Roy Glauber, Harvard University, December 11, 1987.

"Controlling Light by Light," Jamal Manassah, City College in the City of NY, February 12, 1988.

"Coherent Surface Interactions of Spin Polarized Adsorbed ^{131}Xe Atoms," Zhen Wu, Columbia University, February 15, 1988.

"Solitons in Optical Fibers: An Experimental Account," Linn Mollenauer, AT&T Bell Laboratories, February 19, 1988.

"Optical Studies and Other Recent Adventures in II-VI Compound Semiconductor Superlattices," Arto Nurmikko, Brown University, February 29, 1988.

"Ultrafast High-Density Optical Investigations of Quantum Well Structures," Daniel Chemla, AT&T Bell Laboratories, March 4, 1988.

"Photonic Band Structures: The Band Theory of Light in 3D Dielectric Structures," Eli Yablonovitch, Bell Communications Research, April 1, 1988.

"Surface Studies by Non-Linear Optical Techniques," Michael Loy, IBM, April 4, 1988.

"Transient Nonlinear Optical Effects in Electron-Phonon Systems," Masaki Aihara, Yamaguchi University, April 8, 1988.

"Optical Fluctuations and Localization in Random Media," Azriel Genack, Queens College, CUNY, April 15, 1988.

"Optical Switching: An Overview," Paul Liao, Bell Communications Research, April 18, 1988.

"The Ponderomotive Potential of High Intensity Laser Light," Rick Freeman, AT&T Bell Laboratories, April 29, 1988.

"Overview of Silicon Processing at IBM," Randall Isaac, IBM, September 14, 1988.

I. QUANTUM GENERATION AND DETECTION OF RADIATION

1. SILENT LIGHT

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Research Area I, Work Unit 1

We report our progress on silent light in three subsections: (a) theory of solid-state generation of silent light; (b) receiver sensitivity (quantum limit) for silent light; and (c) quantum theory of light detection in the presence of feedback.

(a) Solid-State Generation of Silent Light:[1] We have shown that silent light can be generated as the recombination radiation from semiconductor materials by using a specially designed space-charge-limited light-emitting structure. Silent light is also known as photon-number-squeezed light and sub-Poisson light. The light generated from such a device would be expected to exhibit a small photon-count variance-to-mean ratio (Fano factor) and a large photon flux. The structure could be made small in size and would have the capability of being modulated at a high rate. Such light would be expected to have many uses, from spectroscopy to gravitational wave detection, and possibly to lightwave communications.

(b) Quantum Limit for Silent Light:[2] The performance of lightwave communication system may be experessed in terms of receiver sensitivity. One of the more commonly used measures of sensitivity is the average number of photons per bit $\langle N \rangle$ required to achieve a given bit error rate (BER $\equiv$ Pe), conventionally 10^{-9}. In the absence of background radiation, dark noise, and thermal noise, false alarms are not possible. In this case, the sensitivity of the unity-quantum-efficiency binary on-off keying (OOK) receiver is limited only by the quantum fluctuations of the incident light. In the usual case of laser or LED light, both of which give rise to a Poisson distribution of photons, $P_e = 1/2\exp(-2\langle N \rangle) = 10^{-9}$. This gives the so-called direct-detection "quantum limit" of 10 photons/bit for OOK. However, silent light has a photon-number distribution that is narrower than the Poisson distribution so that the well-known "quantum limit," $\langle N \rangle = 10$ photons/bit, is no longer correct. We have established relationships between the BER and the mean number of photons per bit $\langle N \rangle$, and between $\langle N \rangle$ and the variance-to-mean ratio of the photon number (F), for binomial-distributed silent light.

<N> drops rapidly as F decreases, indicating that improved performance may be expected if silent light is used.

(c) Quantum Theory of Light Detection in the Presence of Feedback:[3] In conjunction with Professors Jeffrey Shapiro of MIT, Bahaa Saleh of Wisconsin, Prem Kumar of Northwestern, and MIT Ph.D. students G. Saplakoglu and S.-T. Ho, we have completed a study directed toward determining the benefits of using feedback in the process of light detection. Initially we extended the usual open-loop semiclassical theory of light detection to include closed-loop operation in which there is feedback from the detector to the source.[4] The revised theory took the form of a self-exciting point process, which could exhibit reduced noise. We have now extended the open-loop fully quantum theory of light detection to include closed-loop operation. We discovered that the unmistakable signatures of nonclassical light associated with open-loop detection, such as sub-Poisson photocounts, do not carry over to closed-loop systems. It turns out that if the open-loop illumination does not require the use of quantum photodetection theory, then neither does the closed-loop illumination. Conversely, if the open-loop illumination is nonclassical, then the closed-loop behavior must be analyzed quantum mechanically. Such feedback can, in general, be useful for generating silent light when photon pairs are available, such as in parametric downconversion.

This research was supported by the Joint Services Electronics Program and by the National Science Foundation, Grant CDR-84-21402.

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2. OPTICAL COHERENT TRANSIENT SPECTROSCOPY

Sven R. Hartmann, Principal Investigator (212) 854-3272

Research Area I, Work Unit 2

A. LUMINESCENCE, ABSORPTION, AND MODULATED ABSORPTION SPECTROSCOPY IN CdS_SSe_{1-x} SEMICONDUCTOR MICROCRYSTALLITES IN GLASS (F. Moshary, E. Usadi, and S. Hartmann)

1. Introduction--Glasses containing CdS_xSe_{1-x} have recently been the focus of a series of experiments investigating quantum confinement and nonlinear optical effects in these systems.[1-6] We have capitalized on the large third order optical nonlinearity of these systems in a series of experiments employing broad-band incoherent time-delayed four-wave mixing for relaxation time measurements in these glasses in the femtosecond time domain. To better understand our experimental results we carried out a series of experiments to characterize the energy level structure of these systems near their absorption edge. We collected luminescence, transmittance, and photomodulated absorption data on a number of Corning colored glass filters containing CdS_xSe_{1-x} with an apparent range of x values at 77 K. In this report we present and discuss experimental results obtained on the filter with transmission characteristic C2-59. This is the same filter that we used for our time-delayed four-wave mixing experiments and also has been the focus of experimental efforts by a number of other groups.[2-4,6] The average size of particles in samples of such glass has been measured to be 90 to 120 Å with a standard deviation of 25 Å.[4] Several values of x (reflecting either measurement uncertainties or variations in composition) have been reported for this particular filter ranging from 0.121 to 0.36.[3,4,6] Based on the measurements by Langer et al.,[7] and the reported range of values for x, the estimated emission edge for the bulk semiconductor is to the longer wavelength side of 6260 Å in our temperature range.

2. Experimental Set-up--The sample was a 1.4 mm-thick C2-59 Corning color filter mounted in a Janis Supertran cryogenic refrigerator and cooled to liquid nitrogen temperature. A Spectra Physics model 170 Ar^+ laser operating at 515 nm was used to pump a Spectra Physics model 370 dye laser. In the luminescence experiments, the Ar^+ 515 nm light was the excitation

source. Filter fluorescence was collected on the same side as the excitation and focused on the input slit of a 0.75 meter Spex spectrometer. The spectrometer was electronically scanned and the fluorescence intensity was recorded as a function of wavelength using an RCA 31034 photomultiplier tube.

For the transmission measurements, the output of the tunable dye laser was split with part of it (the reference beam) incident on a photodiode. The other part (the probe beam) was transmitted through the sample and made to fall on a second photodiode. The transmission coefficient, defined as the ratio of transmitted to reference beam intensity, was then measured as a function of wavelength.

The photoinduced absorption modulation experimental set up was similar to the transmission experiment with a few modifications: 1) A part of the output of the Ar^+ at 515 nm was passed through a chopper to modulate it at 250 Hz. This modulated pump beam then illuminated the sample on the same spot as the dye laser probe beam, affecting the probe's transmission through the sample. 2) The transmitted probe signal was then input to a lock-in amplifier (LIA) phase locked to the chopper. The LIA measured the component of the transmitted probe signal in phase with the pump. The ratio of the LIA output to the reference probe beam was recorded as a function of wavelength. The specifically modulated data were then divided by the unmodulated transmission at each wavelength to give the $\Delta T / T$ photomodulation.

3. Results and Discussion--The luminescence data are displayed in Figure 1. The peak luminescence intensity is at 6025 Å, corresponding to 2.0581 eV, in agreement with Warnock et al.[3] However, the other peak in their data at 6400 Å is absent from ours. They attribute the emission at 6025 Å to bound excitonic recombination in the few, larger, bulk-like fragments.

The transmission data are also displayed in Figure 1. The transmission is approximately 25% at 6025 Å and 50% at 6060 Å. The absorption coefficient α vs. wavelength obtained from the transmission data differentiated with respect to wavelength is plotted in Figure 2. Also plotted in Figure 2 are the direct modulated absorption data. In the differential absorption curve two peaks are visible, at 5930(40) Å and in the 5970 Å-6000 Å region. The

Fig. 1 Luminescence & Transmission
Corning 2-59 filter at 77K

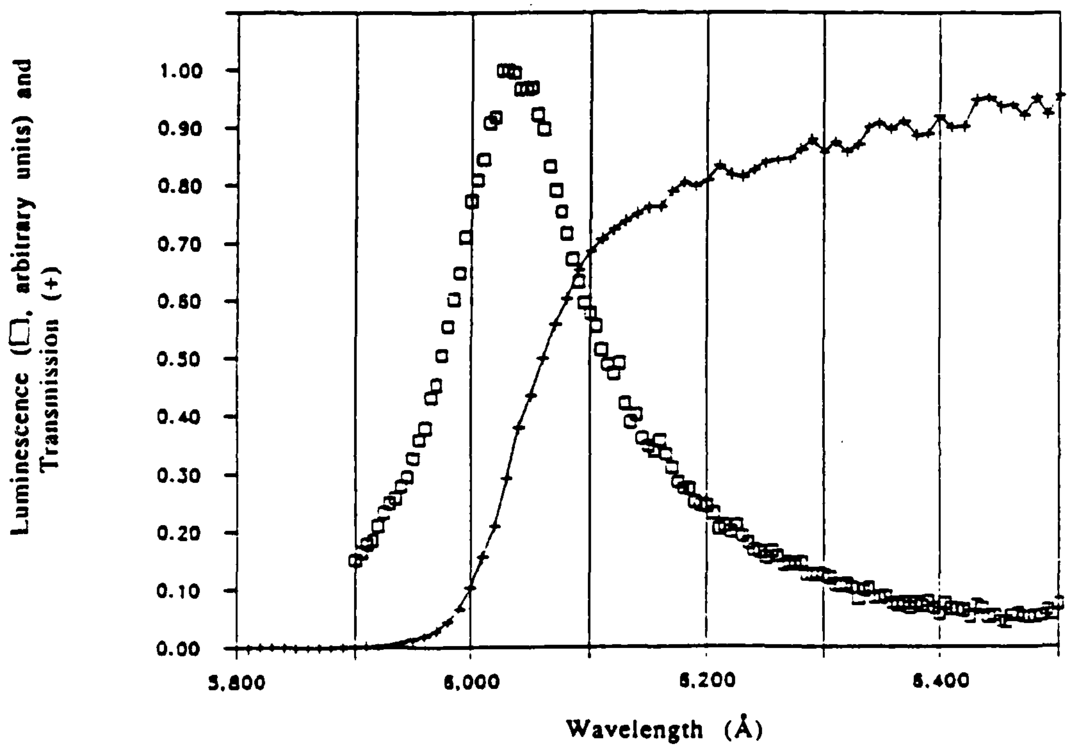

Figure 1

Fig. 2 Modulated & Differential Absorption
(absorption: C2-59 filter at 77K)

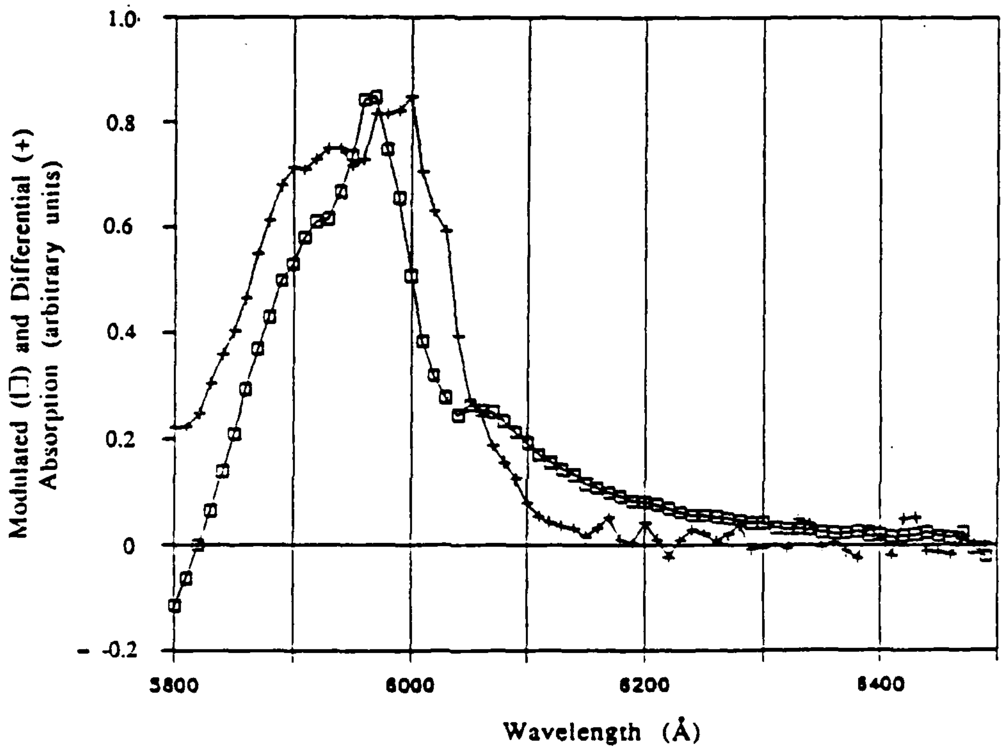

Figure 2

modulated absorption curve has three features at 5920 (30) Å, 5970 Å, and 6050 Å.

Peaks in the differential absorption represent amplitude changes in the absorption spectrum. Based on the work of Thomas et al.[8] and Langer et al.[7] we attribute these peaks to transitions to the A and B excitonic bands. Therefore the energy for a direct transition to the bottom of the excitonic bands at k=0 must be approximately 2.072 eV (±5meV) for band A and 2.089 eV (±2meV) for band B. Thus, the valance band splitting is approximately 17 meV which is close to the 16 meV for bulk CdS.[8]

One can explain the blue-shifted features in the modulated absorption relative to the differential absorption data following a treatment similar to Doyle et al.,[9] which gives (for E=hv):

$$\Delta T/T = \int_0^d \Delta\alpha(E,z)\, dz.$$

The Ar^+ illumination changes the absorption by generating excess carriers. One possible mechanism involves quasi-fermi levels. The pump changes the value of E_F in the fermi distribution f(E) to some new value E'_F. With this perspective, assuming parabolic bands, the maximum of $\Delta\alpha(E)$ is at $E_g+kT/2$. Therefore, a peak in the modulation data would be blue-shifted from the band gap by approximately 10 Å at 77 K. This explains most of the discrepancy between the locations of the first two pairs of features of the two traces in Figure 2. The third peak in the modulated absorption curve, at 6050Å (2.050 eV), which is 27 meV to the red side of the maximum may be attributed to a direct phonon assisted transition to the A excitonic band as described by Thomas et al.[8] and Langer et al.[7] This puts the value of the longitudinal optical (LO) phonon in this system at 27 meV, close to the value for the LO phonon in CSe of 26.6 meV.

Warnock et al.[3] have explained the observed blue-shift of the emission edge between the microcrystallites and the bulk material in terms of the confinement energy of an electron trapped in a potential well. Assuming that the oxide glass may be modeled as an infinitely deep well surrounding the microcrystallites, and including the Coulombic interaction as a perturbation, they have calculated the confinement energy of the electron to be 122 meV, consistent with our data.

4. Conclusion--Emission and absorption edges in the C2-59 Corning color glass filter have been studied with several spectroscopic techniques. The energy level structure of the microcrystallites is very similar to the bulk material except for a blue-shift that may be explained by quantum confinement effects.

In addition to JSEP, this research was supported by the Office of Naval Research, Contracts N00014-88-K-0299 and N00014-78-C-0517.

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B. SPECTROSCOPIC AND RELAXATION STUDIES OF SEMI-CONDUCTOR MICROCRYSTALLITES IN GLASS AND IN ORGANIC DYE MOLECULES IN SOLUTIONS

(F. Moshary, M. Arend, E. Usadi, and S. Hartmann)

1. Introduction--The possibility of the generation of coherent transients from incoherent light was first exploited by Beach et al.[1] for the observation of photon echoes in sodium. Subsequently, a theoretical treatment was presented by Morita et al.[2] demonstrating that a time domain four-wave mixing (TDFWM) experiment with broad band incoherent light has a resolution on the order of the pulse correlation time.

Broad band incoherent light has several advantages over broad band transform-limited ultrashort pulses: 1) Laser systems for generation of ultrashort pulses are expensive, complicated, and difficult to operate. 2) These systems have poor tunability and limited wavelength range. 3) It is difficult to maintain the form of an ultrashort pulse in an optical system.

In a series of experiments in CdS_xSe_{1-x}: Glass (color filters) and Nile Blue dye in solution (ethanol and methanol), we have extended the broad band incoherent TDFWM technique to a time domain on par with the fastest available lasers. Ultrafast (<25 fsec) coherent transients have been observed in these systems making our work one of the fastest time domain experiments to date.

2. Experimental Apparatus--To obtain a very short time resolution, we need an ultra-broadband source of several hundred Ångstroms. We use amplified spontaneous emission from a transversely pumped flow-through cell containing a mixture of DCM and SR640 dyes in ethanol (Figure 1). The cell is pumped with a Q-switched Nd:YAG laser with a pulse width of 7nsec. A mirror is placed to one side of the cell to provide a single pass amplification. This source operates in the same frequency range as a colliding pulse mode-locked dye laser (6250 Å) and the source spectrum is shown in Figure 1. The experimental apparatus is shown in Figure 2. The output of the above source is split in an interferometer with one arm fixed while the other may be moved with a resolution of 50nm using a Melles Griot nanomover. Thus delays as short as 0.33 fsec may be generated between the two pulses. The two pulses are used to perform a TDFWM experiment in the sample. The four-

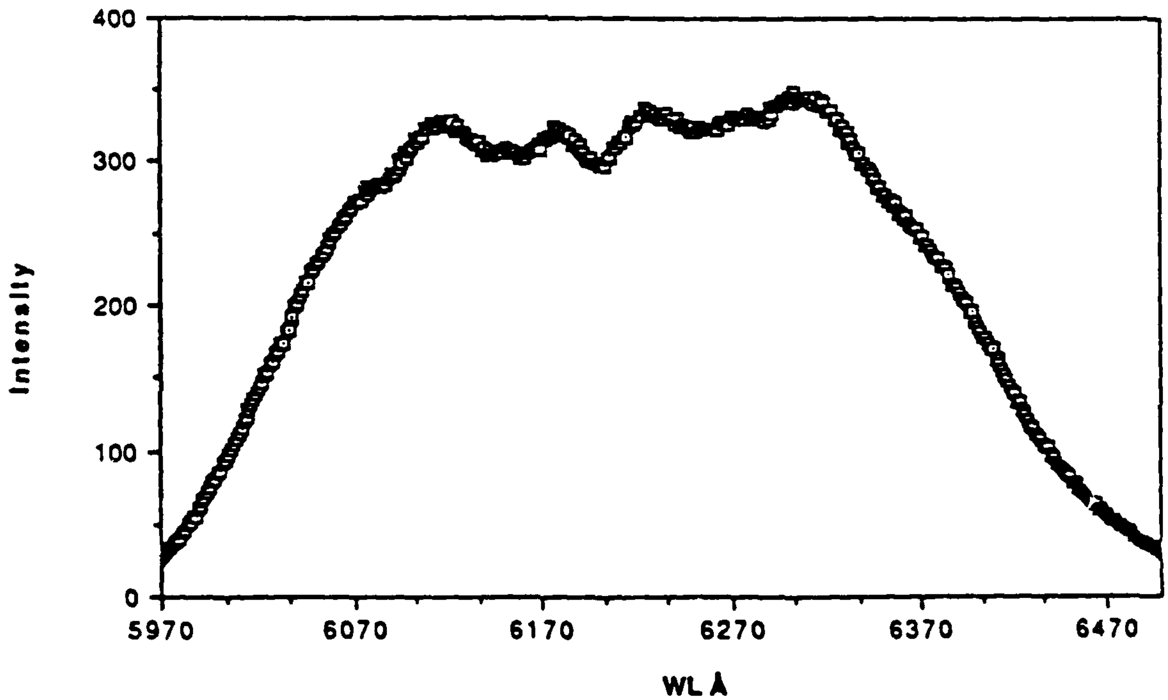

Figure 1. Broad band source and spectral response.

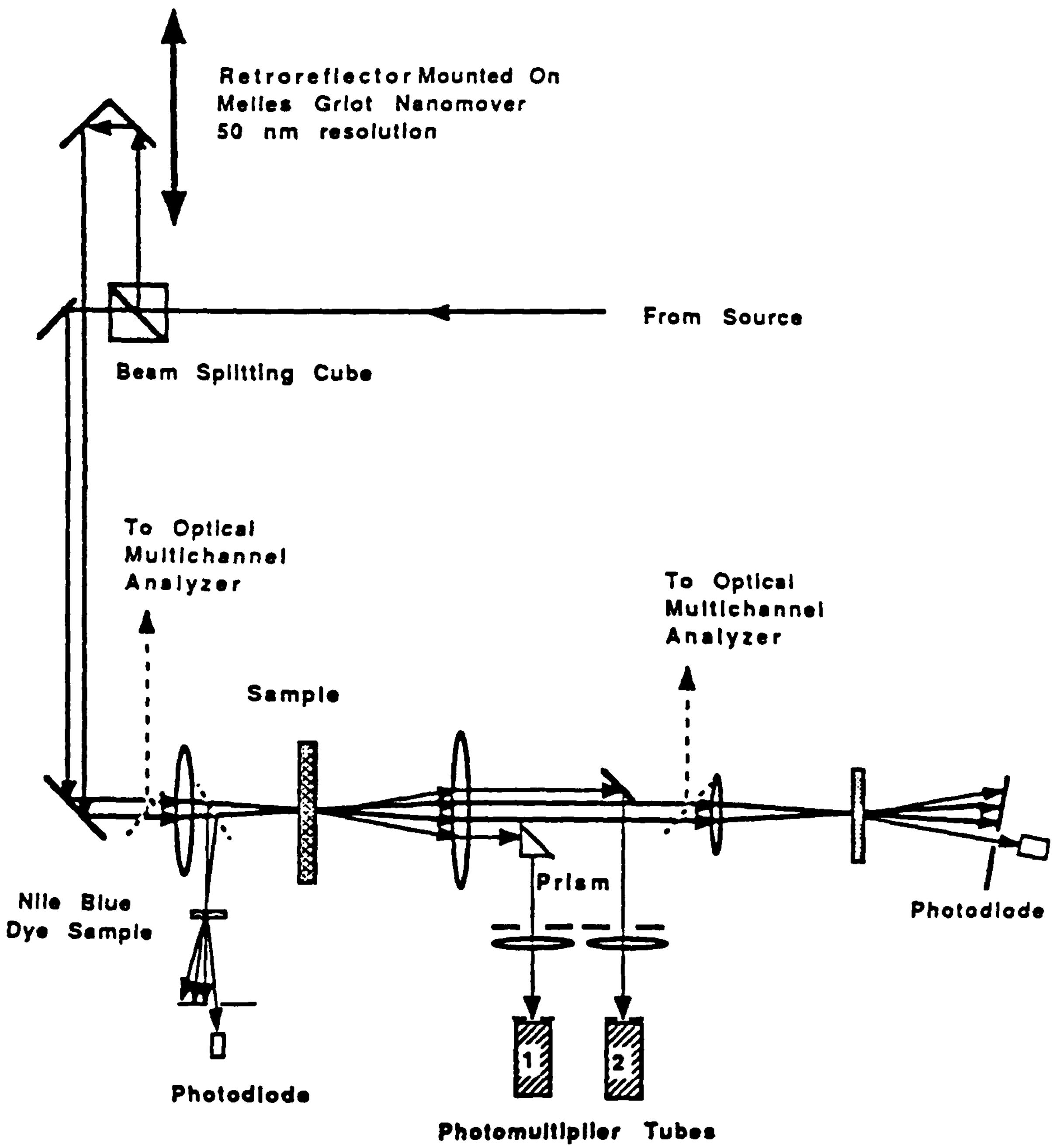

Figure 2. Experimental apparatus.

wave mixing signals in the two phase-matched directions are isolated and recorded as a function of the nanomover position. Source spectra and intensity autocorrelations are simultaneously measured before and after the sample to study its effect on the transmitted light. The sample may be cooled to 4.5 K using a Cryosystems closed-cycle refrigerator. The experiment is controlled by an Apple MacII computer.

3. Theory--For the case where $T_1, t_p >> T_2, t_c$, for pulse length t_p and correlation time t_c, the experiment is formally equivalent to a three pulse scattering experiment with ultrashort pulses. For this case the signal intensity as a function of delay is of the form:

$$I(t) = \int_0^\infty dy \int_0^\infty dy' \int_0^\infty dx \int_0^\infty dx' f(y-y') \exp[-(y+y'+x+x')/T_2] \ldots$$

$$[f(x'-t)g^*(y'-x')+f^*(x'+t)g^*(y'+x')][f^*(x-t)g(y-x)+f(x+t)g(y+x)] \quad (1)$$

where f(t) is the source autocorrelation function and

$$g(t) = \int d\Omega \exp[-i(\Omega_0-\Omega)t]\ G(\Omega)\ d\Omega$$

where $G(\Omega)$ is the inhomogeneous line shape function and the homogeneous line shape is assumed to be Lorentzian. It should be noted that positive delay in one phase matched direction ($2k_2-k_1$) is negative delay for the other direction ($2k_1-k_2$).

If the functions f(t) and g(t) are known, a value for T_2 may be obtained from a simple fit to the data. In general the Fourier transform of the source power spectrum gives f(t) and $G(\Omega)$ may possibly be obtained from an absorption experiment. For a homogeneously broadened system, the above expression simplifies to:

$$I(t) = \left| \int d\Omega \exp(i\Omega t)\ F(\Omega)\ \alpha(\Omega,\Delta\Omega) \right|^2 \quad (2)$$

where $F(\Omega)$ is the power spectrum and $\alpha(\Omega)$ is the absorption function, and $\Delta\Omega$ is the detuning. In this case the signal is symmetric about zero delay.

For an inhomogeneously broadened system the signal is asymmetric about t=0. There is also a shift of the maximum of the integrated signal from

zero delay. For short delays ($t << T_2^* = 1/\Delta_{inh}$), there is no rephasing contribution to the total integrated signal while for longer delays ($t > T_2^*$) the signal is integrated over the dephasing and rephasing of the macroscopic dipole moment. This results in a shift of the maximum of the integrated signal from zero delay. The two graphs in Figure 3 demonstrate the effects of varying T_2 (Fig. 3a) and T_2^*(Fig. 3b) for a given t_c, assuming Gaussian inhomogeneous line shape and Gaussian auto correlation functions. Clearly, variations in T_2 mostly effect the front ($t>0$) side of the traces while variations in T_2^* mostly effect the back ($t<0$) side.

4. Experimental Results--The two systems selected for investigation were: (a) CdS_xSe_{1-x} semiconductor microcrystallites in glass, and (b) Large organic dye molecules in solution.

(a) CdSxSe1-x semiconductor microcrystallites in glass--Corning sharp cut-off color filters consist of semiconductor microcrystallites of average size approximately 100 Å doped in silicate glass.[3] These systems have been of interest for: a) their fast and large third order nonlinearity[4] (of the order of 10^{-8}esu) making them *suitable* candidates for optical signal processing, and b) the possible existence of quantum size effects, and hence their relevance to quantum dot research.[3, 5-7] Additionally these systems are suitable for our experiments since near-band-gap transitions lie in the visible and are easily accessible with a dye laser. Also, T_1 in these systems has been measured to be 16 to 30 psec or longer[3,8,9] while values for T_2 are in the femtosecond regime. These systems are inexpensive and readily available at various thicknesses and colors (band gap energies). Figure 4a is the experimental trace for the .2 mm C2-59 filter at room temperature. Included in Figure 4a is the source intensity autocorrelation for comparison. Since the trace is symmetric about zero delay, the system is homogeneously broadened. Figure 4b shows the theoretical fit to the data for T_2 = 40 fsec using eq. 2. Figures 5a and 5b show the experimental results for 0.7 and 4.0 mm thick C2-59 filters. In comparison to the trace in Figure 4a, these traces are clearly asymmetric about zero delay which is indicative of an inhomogeneously broadened system. Recent experiments in different thickness filters have indicated that a possible explanation for the transition from the homogeneous to the inhomogeneous character is a change in the energy region where the four-wave mixing occurs. As the optical thickness

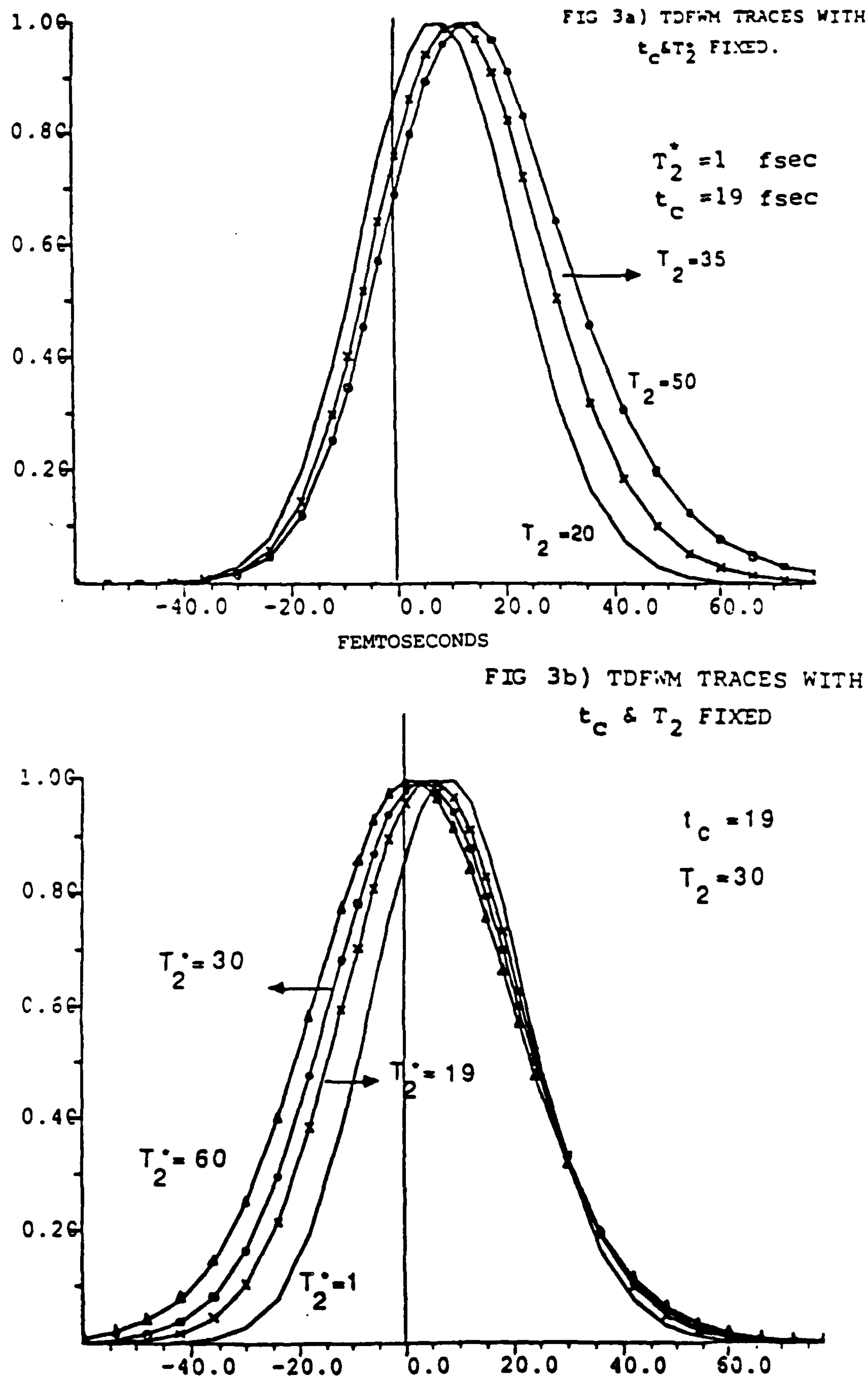
FIG 3a) TDFWM TRACES WITH
t_c & T_2^* FIXED.
T_2^* =1 fsec
t_c =19 fsec
T_2=35
T_2=50
T_2 =20
1.00
0.80
0.60
0.40
0.20
-40.0
-20.0
0.0
20.0
40.0
60.0
FEMTOSECONDS
FIG 3b) TDFWM TRACES WITH
t_c & T_2 FIXED
t_c =19
T_2=30
T_2^*= 30
T_2^*= 19
T_2^*= 60
T_2^*=1
1.00
0.80
0.60
0.40
0.20
-40.0
-20.0
0.0
20.0
40.0
60.0

Figure 3.

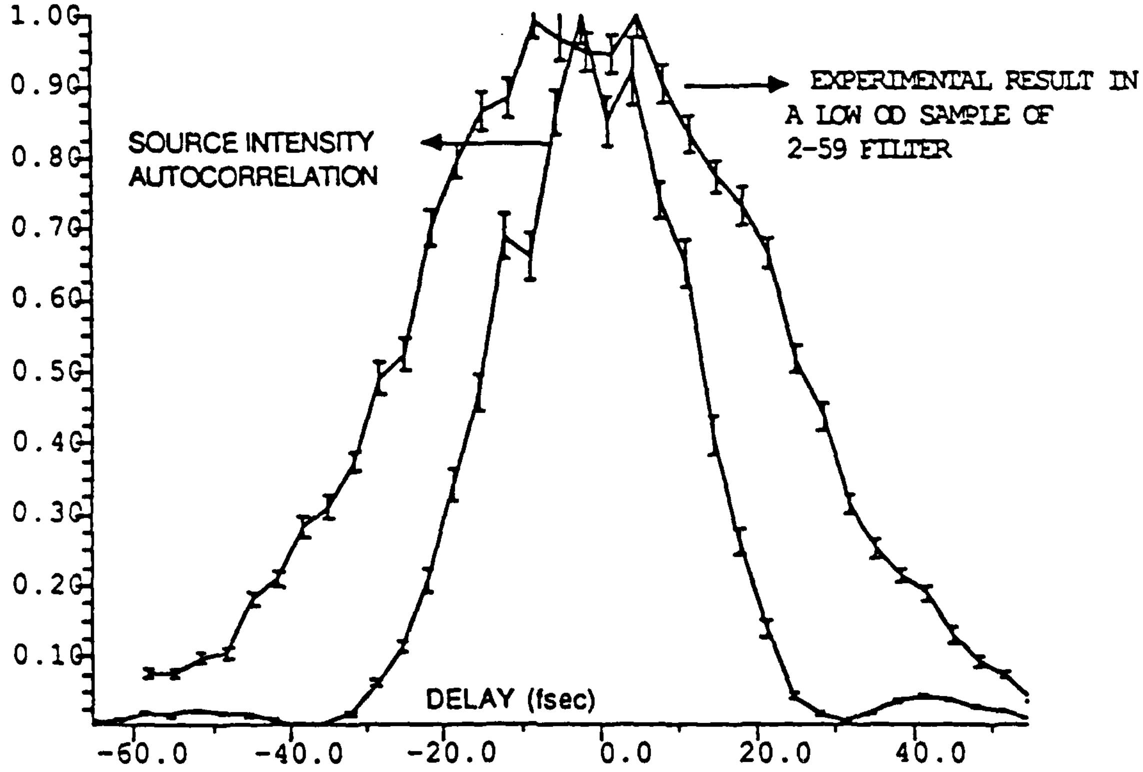

Figure 4(a). TDFWM results in C2-59 filter (0.2mm) & intensity AUTOCORR.

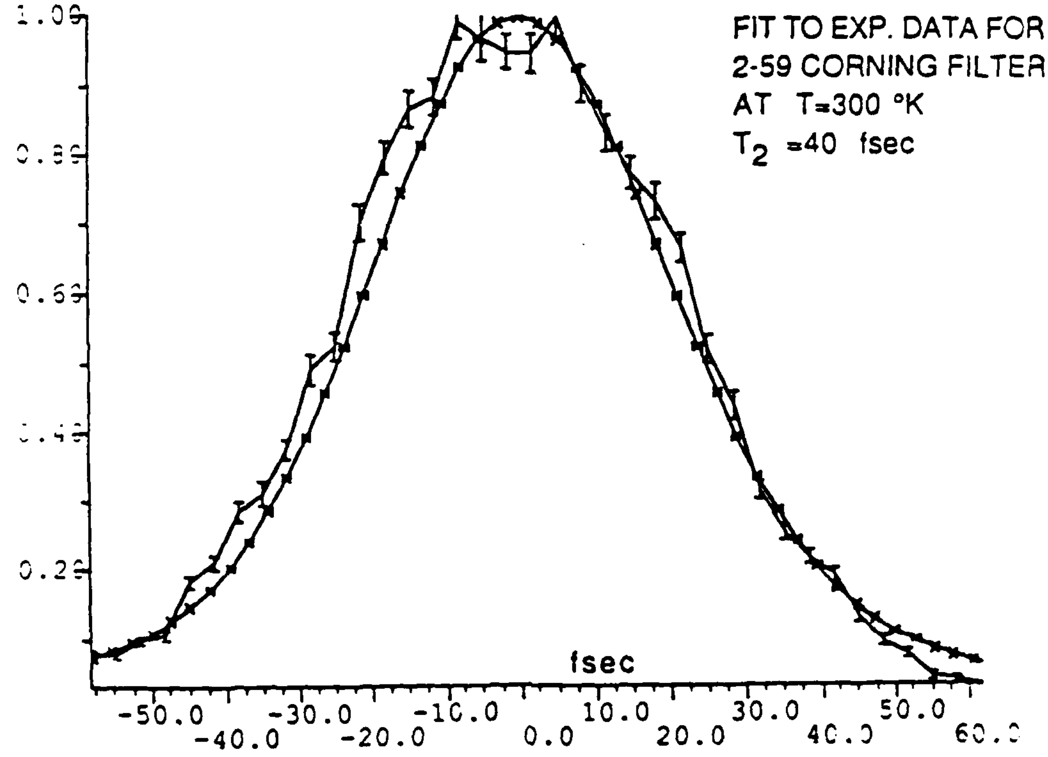

Figure 4(b). Theoretical fit to C2-59 (0.2 mm) data.

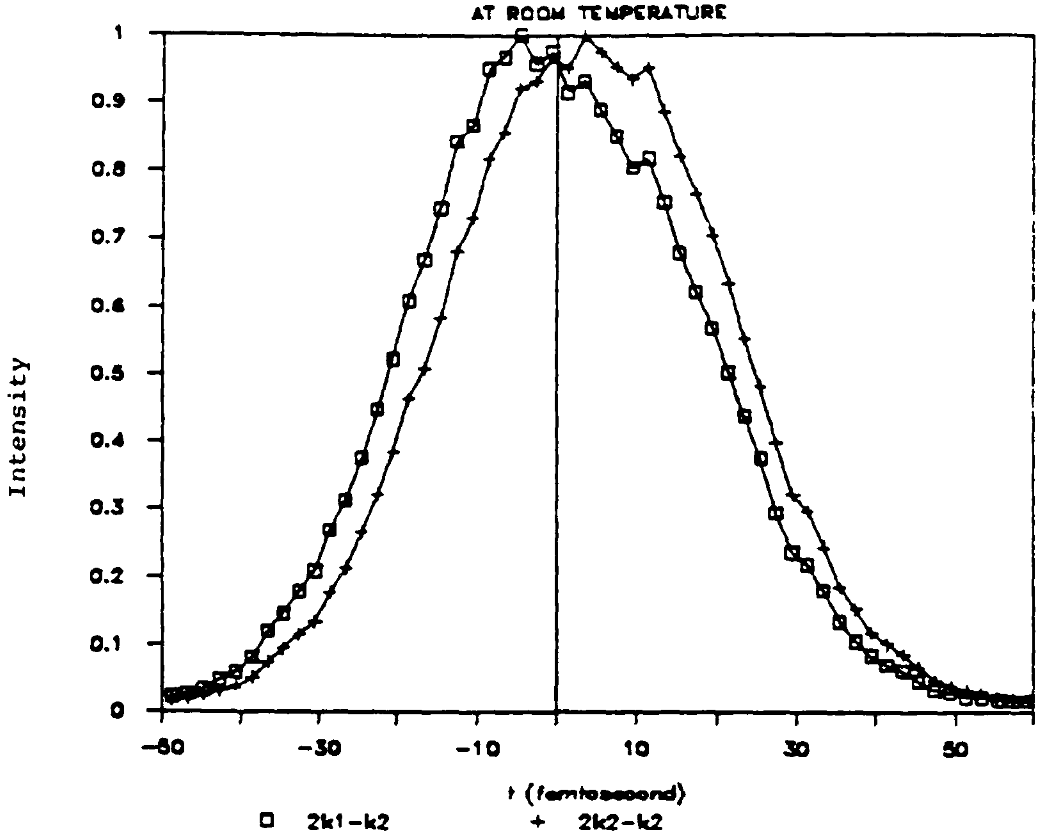

Figure 5(a). TDFWM in 0.7 mm C2-59.filter.

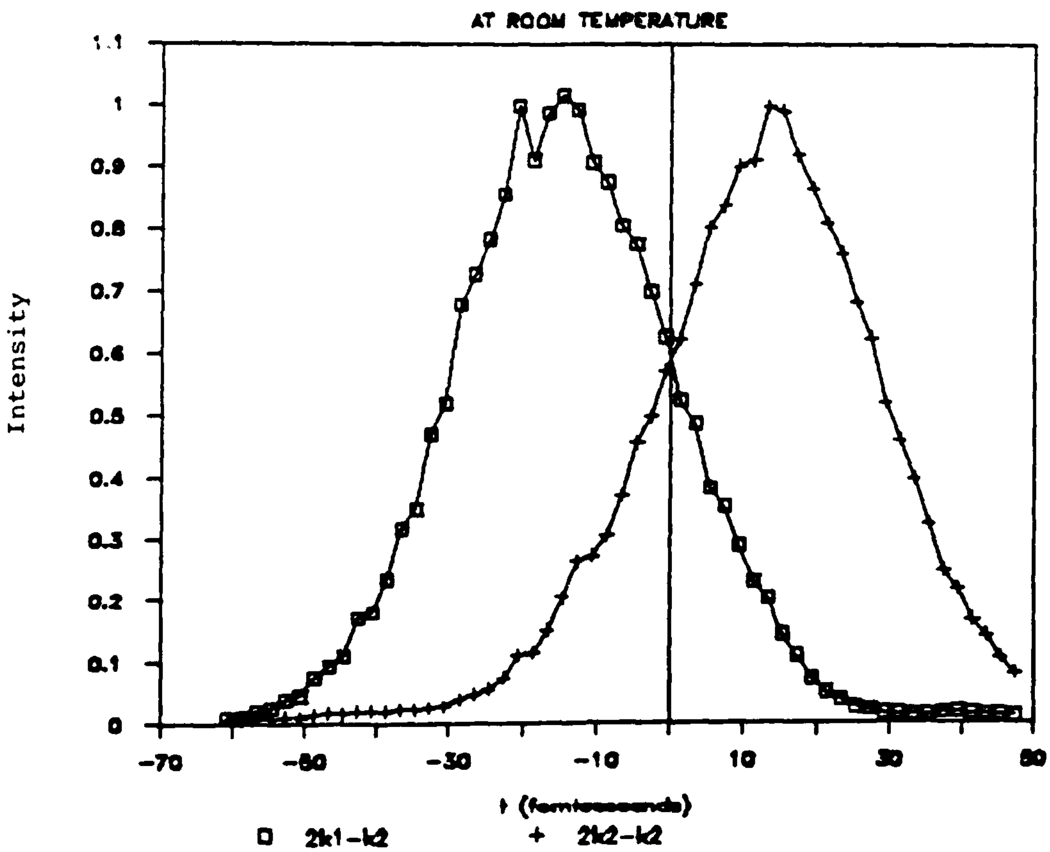

Figure 5(b). TDFWM in 4mm C2-59 filter.

is increased the signal is more due to the lower energy transitions, i.e. transitions at or below the band gap. Therefore, the nature of the broadening changes in the system as a function of electronic energy

(b) Organic dye molecules in solution--These systems have been of much experimental interest in the past. Relaxation mechanisms in these systems have been studied by techniques such as four-wave mixing[10,11] and spectral hole burning experiments.[12] They are highly nonlinear and have long ground-state recovery times (nsec to msec) while phase relaxation times in these systems are extremely fast (fsec). In fact, a measurement of the T_2 value in these systems at room temperature has not been made to this date.

The experimental traces obtained for Nile Blue in ethanol at room temperature are symmetric about zero delay and the same as the autocorrelation function calculated from the observed spectrum. This is clearly indicative that the phase relaxation is faster than our resolution of a few fsec. A similar experiment at 4.5 K yields a totally different result (Figure 6a). At this temperature, the experiments with either parallel or perpendicularly polarized pulses produce the same results, and optical thickness does not have the same effects here as with the color filters. Preliminary analysis assuming $T_2^* = 0$ (eq. 3) indicates the value of T_2 in this system to be under 10 fsec (Figure 6b). The fit in Figure 6b is in reasonable agreement with the experimental results for the front side (positive delays). We believe the mismatch on the back side (negative delays) to be due to the assumption that $T_2^* = 0$. Numerical computations are currently in progress to get a value for T_2^* that will give a better fit for negative delays.

5. Conclusion--Utilizing a broadband incoherent time-delayed four-wave mixing technique, we have easily observed ultrafast coherent transients in a time domain that is not accessible to any but the fastest lasers today. We have measured T_2 values under 10 fsec which are the shortest reported to date. In addition to making ultrafast time domain phase relaxation measurements readily accessible, this technique can also indicate whether the system under investigation is homogeneously or inhomogeneously broadened. For the latter case, one can get an estimate for the value of T_2^* by fitting the data for negative delays.

In addition to JSEP, this research was supported by the Office of Naval Research Contracts N00014-88-K-0299 and N00014-78-C-0517.

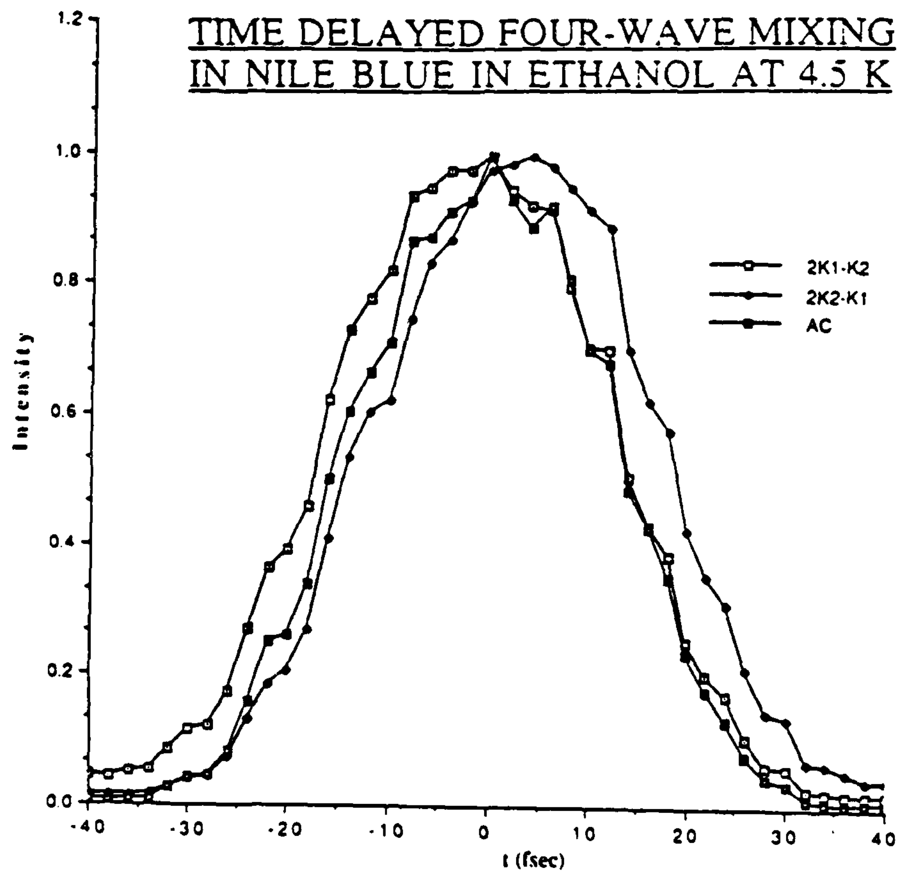

Figure 6(a). TDFWN traces & intensity autocorr. (AC).

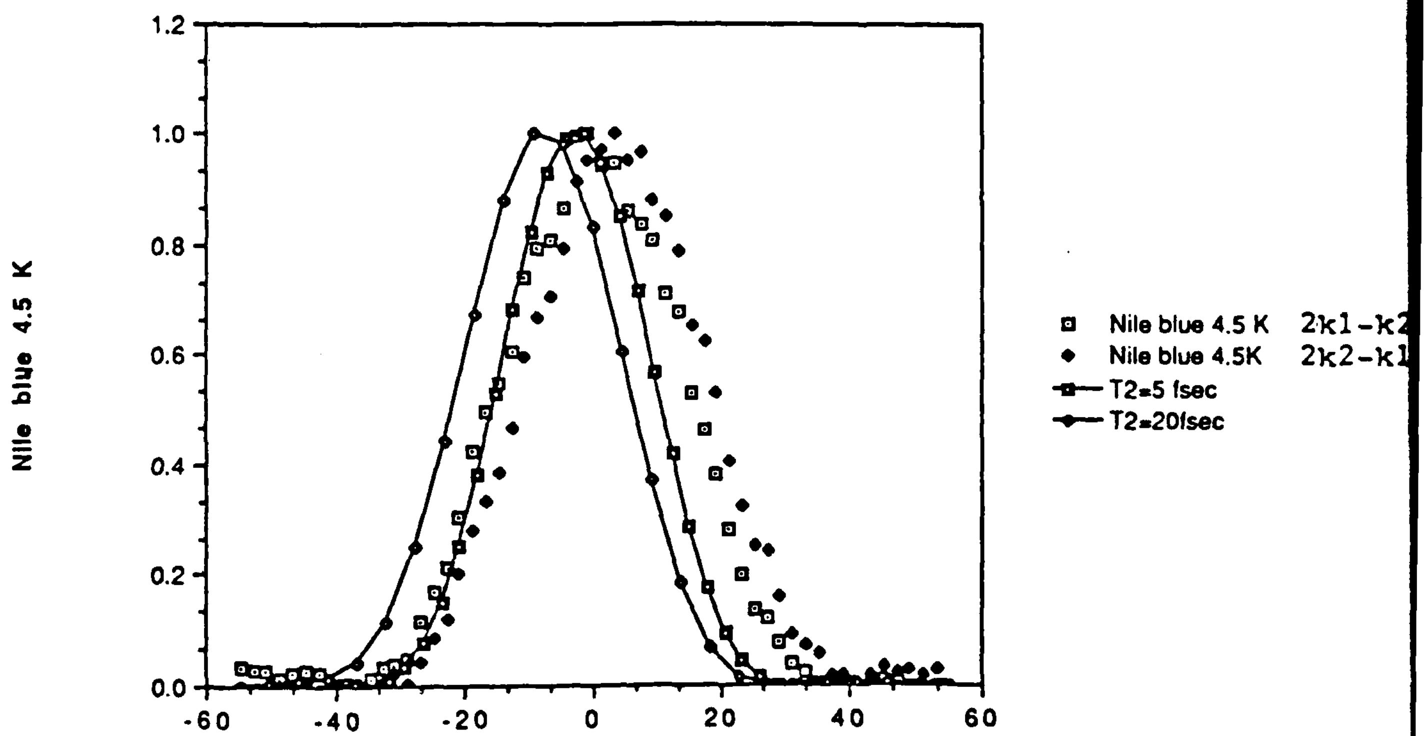

Figure 6(b). Fit to 2k1-k2 trace with $T_2^* = 0$.

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C. ATTOSECOND BEATS IN SODIUM AND POTASSIUM VAPOR

(D. P. DeBeer, E. Usadi, and S. R. Hartmann)

1. Introduction and Summary of Background Work--In several recent time-delayed four-wave mixing (TDFWM) experiments on the sodium D doublet, we studied the amplitude modulation of scattered light beams as a function of time delay between input pulses. In the first of these experiments,[1] the first order four-wave mixing signal modulated with a frequency* equal to the difference between the doublet frequencies.

Then, employing a novel geometry for the input laser beams, we observed a modulation of the first order signal corresponding to the sum of the doublet frequencies.[2] The sum frequency of the sodium D lines is 1.02×10^{15} Hz; thus the period* of modulation is in the attosecond (10^{-18} sec) regime. We believe this is the fastest such modulation yet observed. One goal of present work is to observe a still faster modulation.

Finally, we observed the modulation of higher-scattering-order four-wave mixing signals (Figure 1) for each of the two geometrical arrangements.[2] For the difference frequency case, the higher-order signals contained modulation components at integral multiples of this difference frequency. This is apparent in the data shown in Figure 2. The first-order signal modulates as a $(\sin)^2$ function, but the higher-order signal displays modulation with sharper peaks. We believe this should be true in the sum frequency case as well. However, the expected narrowing of the modulation peaks was unobservable due to instabilities in the apparatus. Another goal of our present work is to observe the narrowing described above in the sum frequency case.

One prediction of our theoretical analysis which has not yet been observed is that the modulation peaks for all scattering orders, including the first, will narrow in the limit of large pulse areas. This we also hope to investigate in our present work.

*This modulation occurs not in real time, but in terms of the time delay between input pulses. "Frequency" and "period" should be understood accordingly.

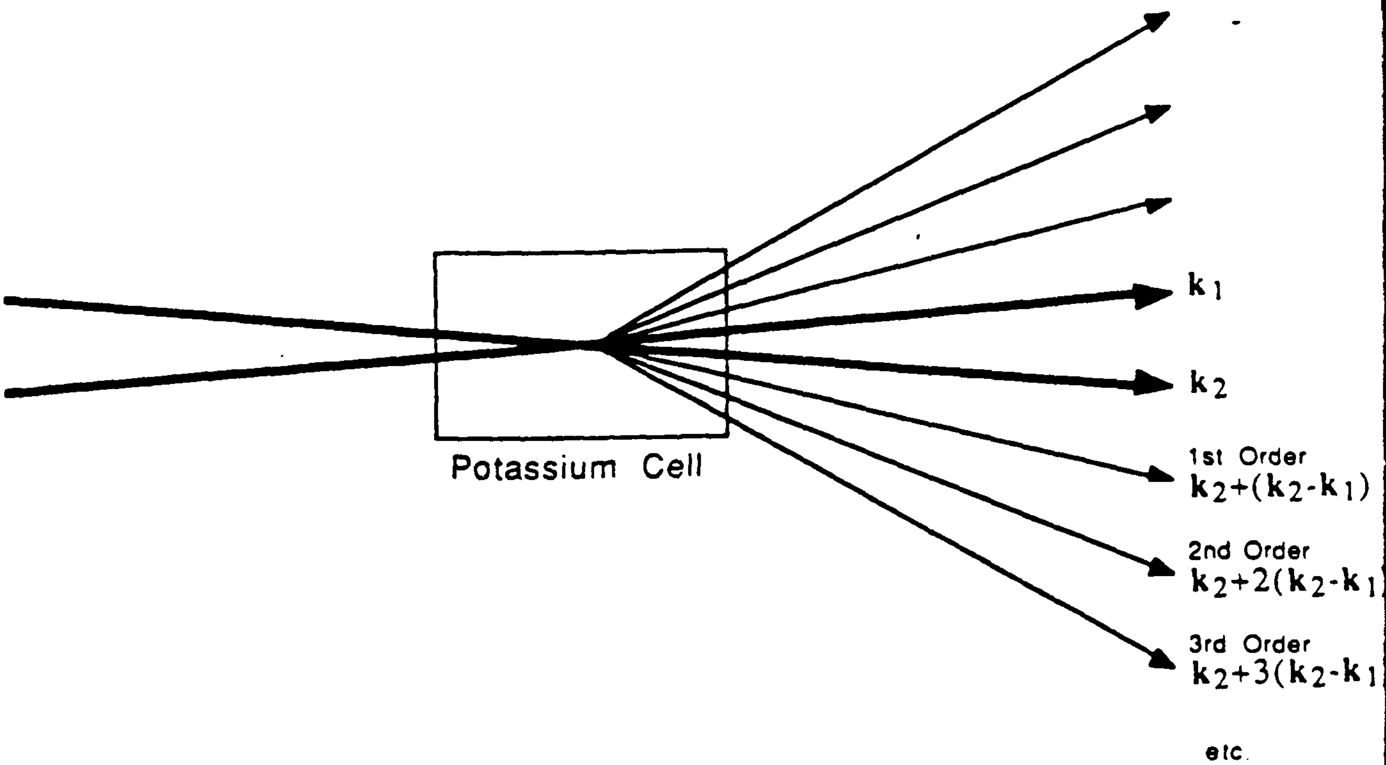

Figure 1. Geometry of four-wave mixing scattering, showing the directions of the different scattering orders relative to the input beams $\mathbf{k}_1$ and $\mathbf{k}_2$.

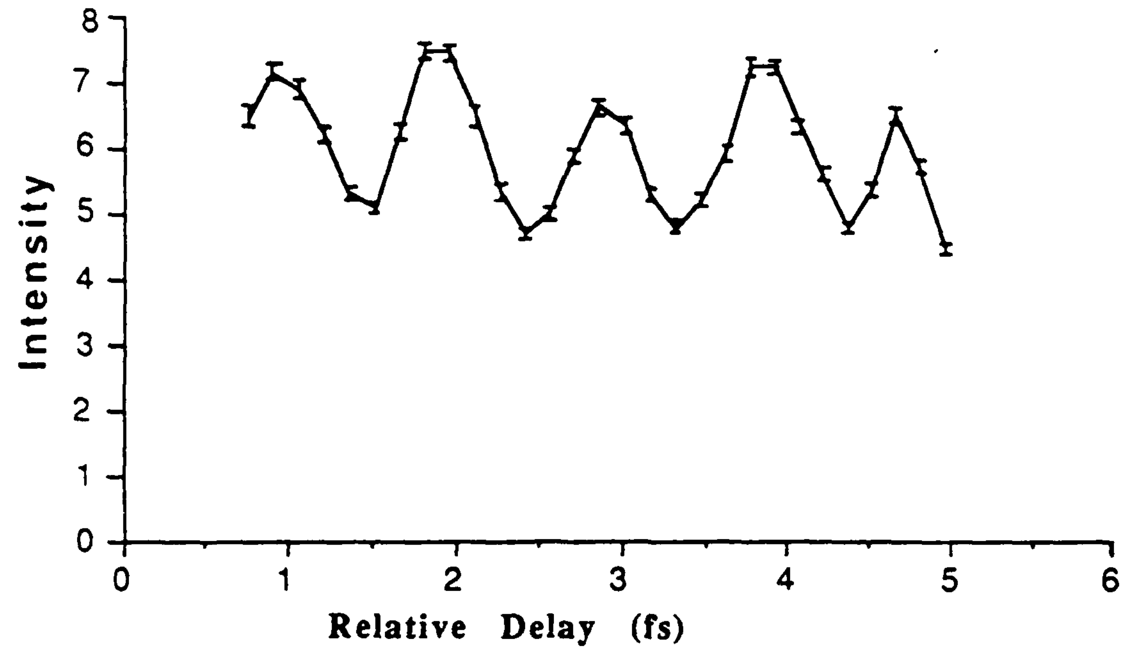

Figure 2(a). Typical set of data for the sum-frequency geometry: signal intensity vs relative pulse delay.

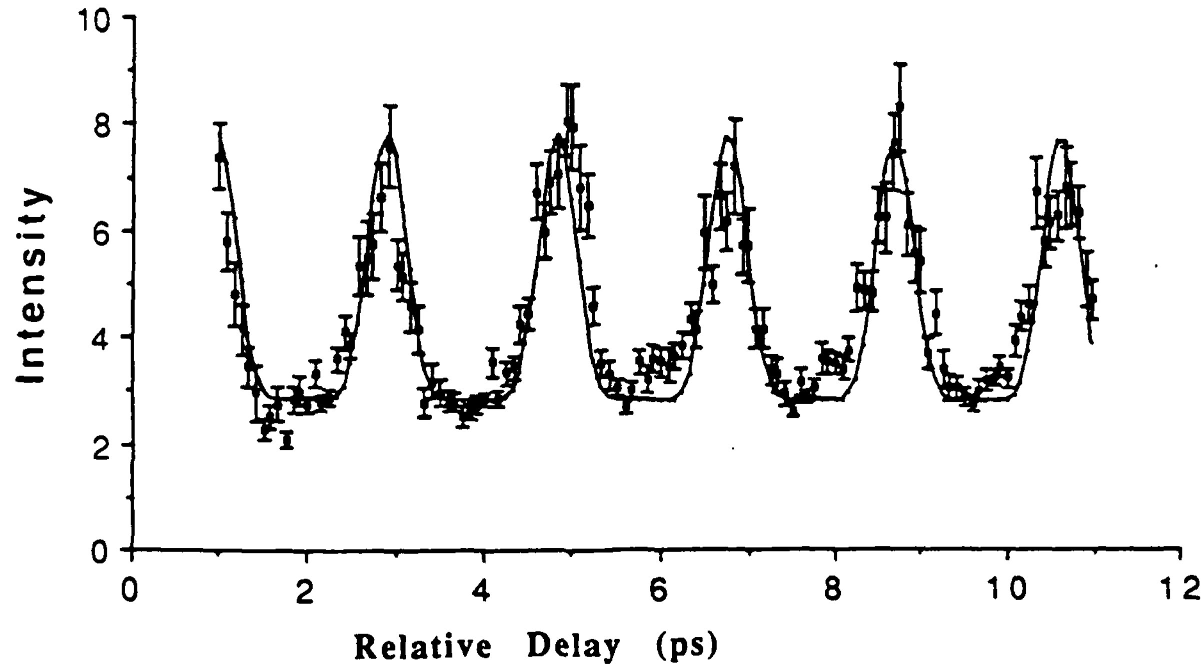

Figure 2(b). Data taken in the difference-frequency geometry showing the narrowing of the modulation in a high diffraction order (n=4).

Figure 2

2. Sum Frequency Beats: Theory--The excitation field takes the following form:

$$E = E_0\{e^{-i\Omega t}\left[e^{ik_1 \bullet r} + e^{ik_2 \bullet r - i\Omega\tau}\right] + e^{-i\Omega' t}\left[e^{ik'_1 \bullet r} + e^{ik'_2 \bullet r - i\Omega'\tau}\right]\}$$
$$+c.c. \qquad (1)$$

We assume the atom is a three level system whose levels are sufficiently separated so that the resonant excitations are effectively isolated. Then the time evolution of the induced polarization is calculated to be:

$$\mathcal{P}(t) = \left[P\Omega_R \sin\left(\Omega(t-\tau) - k_2 \cdot r\right) + P'\Omega'_R \sin\left(\Omega' t - k'_1 \cdot r\right)\right]\frac{\sin ft}{f}$$

$$\text{where } f^2 = 4\Omega_R^2\left\{1 + \cos\left[\frac{\Omega+\Omega'}{2}\tau\right]\cos\left[\frac{\Omega'-\Omega}{2}\tau + (k_2 - k_1)\cdot r\right]\right\}. \qquad (2)$$

P and P' are the dipole moments for the Ω and Ω' transitions, and Ω_R and Ω'_R are the associated Rabi frequencies. We adjusted the optics so that $k_1 - k_2 \cong k'_1 - k'_2$. (For the difference frequency case, the optics were adjusted so that $k_1 - k_2 = -(k'_1 - k'_2)$.) Setting $\Omega'_R = \Omega_R$ and considering only the terms phased to radiate in the directions $k_2 + n(k_2 - k_1)$ $(n > 0)$ we have:

$$\mathcal{P} = \sum_{n=1}^{\infty} \mathcal{P}_n$$

where

$$\mathcal{P}_n(t) = \left\langle \frac{\cos(n\varphi)\sin\left[2\Omega_R t\sqrt{1+\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)\cos\varphi}\right]}{2\sqrt{1+\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)\cos\varphi}} \right\rangle$$
$$\left\{P\sin\left[\Omega(t-\tau) - (k_2 + n(k_2 - k_1))\cdot r - n\frac{\Omega'-\Omega}{2}\tau\right]\right.$$
$$\left. + P'\sin\left[\Omega' t - (k'_1 + n(k_2 - k_1))\cdot r - n\frac{\Omega'-\Omega}{2}\tau\right]\right\} \qquad (3)$$

The brackets <···> indicate an average over the variable φ. For fixed φ the n^{th} component, $\mathcal{P}_n$, of the induced dipole moment, $\mathcal{P}$, is a periodic function of $(\Omega'+\Omega)\tau$ with period 4π. However on averaging over φ the moment $\mathcal{P}_n$ becomes

an (odd/even) function of $\cos\left[\frac{\Omega+\Omega'}{2}\tau\right]$ when n is (odd/even). As a consequence $\mathcal{P}_n^2(t)$ (the output signal) is an even function of $(\Omega'+\Omega)\tau$ with period 2π. In addition, the output signals have the same modulation whether one looks at either Ω or Ω' separately or at both simultaneously.

The detailed behavior of $\mathcal{P}_n$ is readily obtained in the limit of either small or large pulse area $\Omega_R t$. Working first in the small angle limit and keeping only the lowest-order term radiating at Ω we have:

$$\mathcal{P}_n(t) = (-1)^n \frac{2^n}{(2n+1)!}(\Omega_R t)^{2n+1} \cos^n\left(\frac{\Omega'+\Omega}{2}\tau\right)$$

$$\times P \sin\left[\Omega(t-\tau) - (\mathbf{k}_2 + n(\mathbf{k}_2 - \mathbf{k}_1)) \cdot \mathbf{r} - n\frac{\Omega'-\Omega}{2}\tau\right]. \tag{4}$$

The radiated intensity emitted into the n^{th} order is thus:

$$\begin{aligned} I_n &\propto \int (\mathcal{P}_n^* \cdot \mathcal{P}_n)\, dt \\ &\propto \left[\cos\left(\frac{\Omega+\Omega'}{2}\tau\right)\right]^{2n} \\ &\propto \left[\tfrac{1}{2} + \tfrac{1}{2}\cos((\Omega+\Omega')\tau)\right]^n . \end{aligned} \tag{5}$$

As the scattering order n increases, the scattering signal width, measured by the value of τ for which I_n decreases to 1/2, decreases. No higher frequency beat terms are directly observable; the sum frequency beats dominate to all orders of scattering. In the limit of large pulse areas, $\Omega_R t >> 1$, Eq. 3 yields a sharpened modulation pattern which narrows with increasing pulse area and is independent of n for moderate n.

We write below a general expression for $\mathcal{P}_n$.

$$\mathcal{P}(t) = P \sin\left[\Omega(t-\tau) - (\mathbf{k}_2 + n(\mathbf{k}_2 - \mathbf{k}_1))\cdot \mathbf{r} - n\frac{\Omega' - \Omega}{2}\tau\right]$$

$$\times \begin{cases} 0 & \text{for } (\Omega' + \Omega)\tau = \pi, 3\pi, 5\pi, \ldots \\ \dfrac{(-1)^{\eta}}{\sqrt{8}} J_0\left(2\Omega_R t \dfrac{\Omega' + \Omega}{2}\tau\right) & \text{for } (\Omega' + \Omega)\tau \equiv 0, 2\pi, 4\pi, \ldots, 2\lambda\pi, \ldots \\ & \text{where} \begin{cases} \eta = n \text{ if } \lambda \text{ is even} \\ \eta = 0 \text{ if } \lambda \text{ is odd} \end{cases} \\ & \text{otherwise} \\ \dfrac{1}{\sqrt{2\pi\Omega_R t \cos\left(\frac{\Omega' + \Omega}{2}\tau\right)}} \left\{ \begin{array}{l} \dfrac{\sin\left(2\Omega_R t\sqrt{1-\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)} + \frac{\pi}{4}\right)}{\sqrt[4]{1-\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)}} \\ + \dfrac{\sin\left(2\Omega_R t\sqrt{1+\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)} + \left(n - \frac{1}{4}\right)\pi\right)}{\sqrt[4]{1+\cos\left(\frac{\Omega'+\Omega}{2}\tau\right)}} \end{array} \right\} & \end{cases} \quad (6)$$

The character of the last expression is determined by the fact that the average over φ in Eq. 3 is dominated by contributions near $\varphi=0$ and $\pm\,\pi$.. The scattering half-width τ_w is determined by the condition $J_0(x) = 1/\sqrt{2}$ so that $(\Omega'-\Omega)\tau_w = 1.52/\Omega_R t\sqrt{2}$ independent of n. For a pulse area $\Omega_R t \approx 10\pi$ the modulation spikes will narrow to one-hundreth of the modulation period. It is important to note that these peaks reach an asymptotic value and do not dissappear in the large pulse area limit. In the valleys between the peaks the polarization tends to zero as $1/\sqrt{\Omega_R t}$. This result implies that sharp modulation patterns will appear in experiments using cw lasers.

3. Present Work--We are now investigating modulation of four-wave mixing signals in potassium vapor. The apparatus for the sum-frequency experiment is shown in Figure 3. The atomic transition we have chosen is the 4S-6P doublet, which has an average wavelength of 344.69 nm and a splitting of 0.1 nm. Therefore the sum frequency is 1.74×10^{15} Hz. This implies a

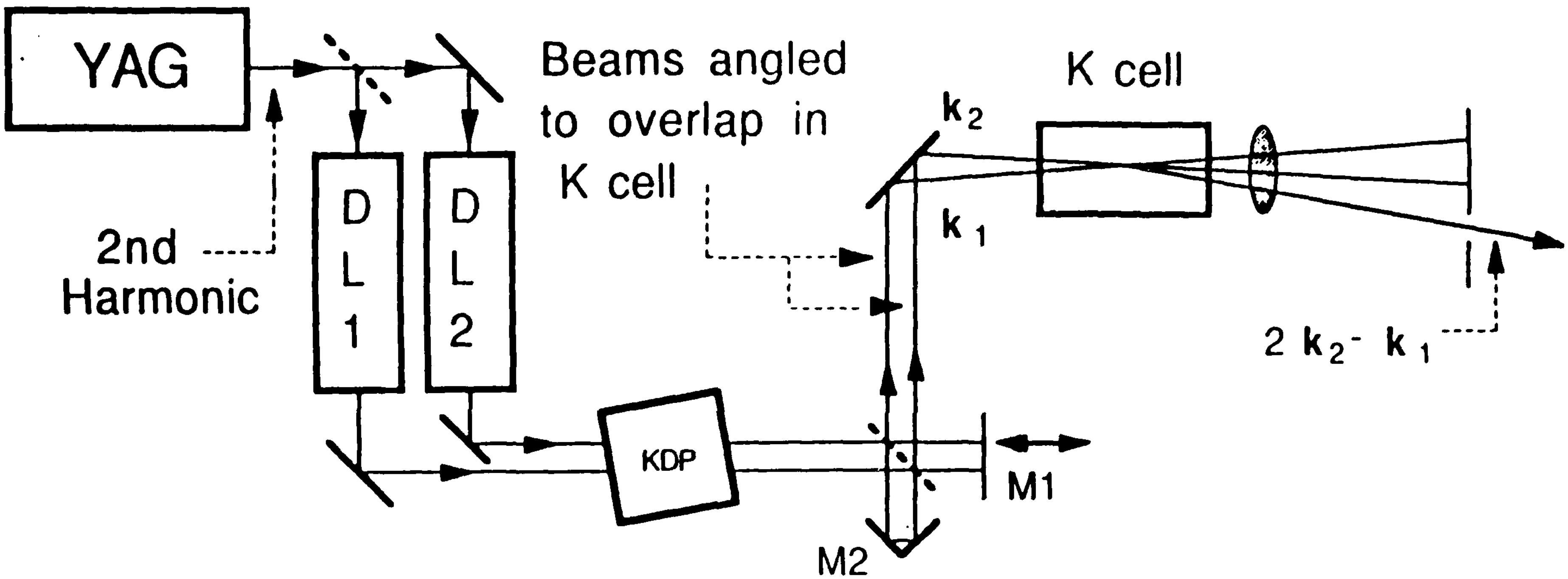

Figure 3. Schematic diagram of apparatus used to generate TDFWM in the sum-frequency geometry (for n=1). The KDP crystal doubles the frequency of each of the laser beams. All subsequent optical components are coated to reflect only these second harmonic UV beams, so no residual visible light reaches the potassium cell. M1 is mounted on a piezoelectric-driven translation stage. M2, made of two perpendicular mirrors, displaces each beam so that it combines at the beam splitter with the beam of the other frequency.

modulation period of 574 attoseconds, nearly twice as fast as the sum frequency modulation in the sodium experiment.

We also plan to repeat the experiment in sodium using cw laser excitation. This will facilitate our study of the four-wave mixing signal modulation behavior in the large pulse area limit.

4. Summary--In the experiments described, the modulations of time-delayed four-wave mixing signals occur in a well-defined manner as a translation stage is moved ultra-short distances. Therefore the existence of sum-frequency beats and their narrowing with scattering order and excitation intensity holds some promise for the development of more accurate position transducers. Furthermore, this work is of fundamental interest in the burgeoning field of short-pulse physics. As faster processes are studied, broader bandwidth excitations will be used which will in turn couple multiple transitions, resulting in complex signal modulations. Sum and difference frequency geometries may be separately employed to untangle confusing spectroscopic details.

In addition to JSEP, this work was also supported by the U. S. Office of Naval Research (Contracts N00014-88-K-0299 and N00014-78-C-0517).

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II. SOLID-STATE ELECTRONICS (MATERIALS AND PROCESSING)

1. ELECTRONIC STATES AT METAL/SEMICONDUCTOR INTERFACES

Edward S. Yang, Principal Investigator (212) 280-3103
Research Area II, Work Unit 1

A. CONTROL OF THE SCHOTTKY BARRIER USING AN ULTRATHIN INTERFACE METAL LAYER

(X. Wu, M. T. Schmidt and E. S. Yang)

The metal-semiconductor contact as a basic structure in microelectronics has received wide attention for many years. Particularly at the present time, MESFET's remain the most popular device in GaAs technology. Controlling the barrier height, so as to tailor the threshold voltage, is a major challenge in GaAs device fabrication. However, for ordinary Schottky contacts having a single metal in contact with the semiconductor, the barrier height is fixed, i.e., its value is determined by the contact metal and the substrate semiconductor. Although some processing conditions could affect the barrier height to a certain extent,[1] most of them are not well-controlled. In this report, we present a new kind of Schottky diode which shows potential in this application. The device involves two different metal overlayers with one on top of the other. The inner metal layer is thin and in intimate contact with the semiconductor. Its thickness ranges from 0 to 50 Å. The outer layer metal is thick and is fixed at 400 Å. It is found that the Schottky barrier height of these devices varies from the value associated with the outer metal to that belonging to the inner metal. This novel result shows us that controlling the Schottky barrier height in a wide range is practical. With different inner layer thickness and a proper combination of metals, we can virtually obtain any prespecified barrier height value from the highest to the lowest available on a continuous basis. This will certainly be very useful for MESFET fabrication and other device applications. In addition, the experiment reveals a new approach to study the fundamental metal-semiconductor interface properties. The data of barrier height versus the inner layer thickness discloses two pieces of valuable information. One is the Thomas-Fermi screening length[2] of the metals and the other is the density of states distribution at these particular metal-

semiconductor interfaces. The details of the theory will be published elsewhere.[3] Here we report the experimental results.

The diodes were fabricated on a GaAs (100) substrate which was nominally undoped with $n = 10^{16}$ cm^{-3}. We chose Pt and Ti as the two contact metals. Pt is known to have the highest barrier height on GaAs, 0.97 eV, whereas Ti has a lower barrier height of 0.77 eV. This combination could be anticipated to produce a large barrier height variation. The structure of the bimetal Schottky diode is shown in the inset of Figure 1, where Metal A represents the thin inner metal and Metal B denotes the top thick metal. The thickness of Metal A varies from 0 to 50 Å, while Metal B is always 400 Å thick. Ohmic contacts were formed on the backside of the substrate by melting indium onto a Mo plate. Before this, the sample was degreased with TCE, acetone and methanol followed by two chemical cleaning procedures: a) $NH_4OH:H_2O_2:H_2O$ (20:7:973) for 1 min; b) $H_2SO_4:H_2O_2:H_2O$ (10:1:1) for 1 min. After rinsing in DI water, the sample was mounted onto the Mo plate and immediately loaded into the UHV evaporation chamber, where the vacuum pressure was kept < 10^{-7} Torr. Prior to the metallization, the sample was heated *in situ* to 550°C for 5 min to desorb the chemically formed oxide on the sample surface and to anneal the indium back contact as well. Samples prepared this way have shown no oxygen contamination by XPS detection.[4,5] The metallization was carried out by e-beam evaporation at room temperature. A fixed Mo shadow mask was attached to the front of the GaAs surface containing 4X4 open dots. Each dot was 1 mm in diameter. A movable blank mask allowed us to stepwise deposit four different thicknesses of Metal A on one substrate. This technique not only saved a great deal of time, but also reduced the experimental errors due to the inaccuracy of the crystal thickness monitor and the fluctuation of the substrate surface conditions. After the first-layer metal (Metal A) was deposited, some of the samples directly proceeded to the next step while others were subjected to a 300°C *in situ* annealing for 1 min. They were then cooled down to room temperature and the second layer (Metal B) was evaporated.

Two sets of samples were made in this study using Pt and Ti. The first one used Ti as Metal A and Pt as Metal B and is referred to as the Pt/Ti/GaAs sample. The second set interchanges the positions of the Pt and the Ti and is denoted as the Ti/Pt/GaAs sample. This gives us a good comparison of the interface properties between the two metals. The Schottky barrier heights of

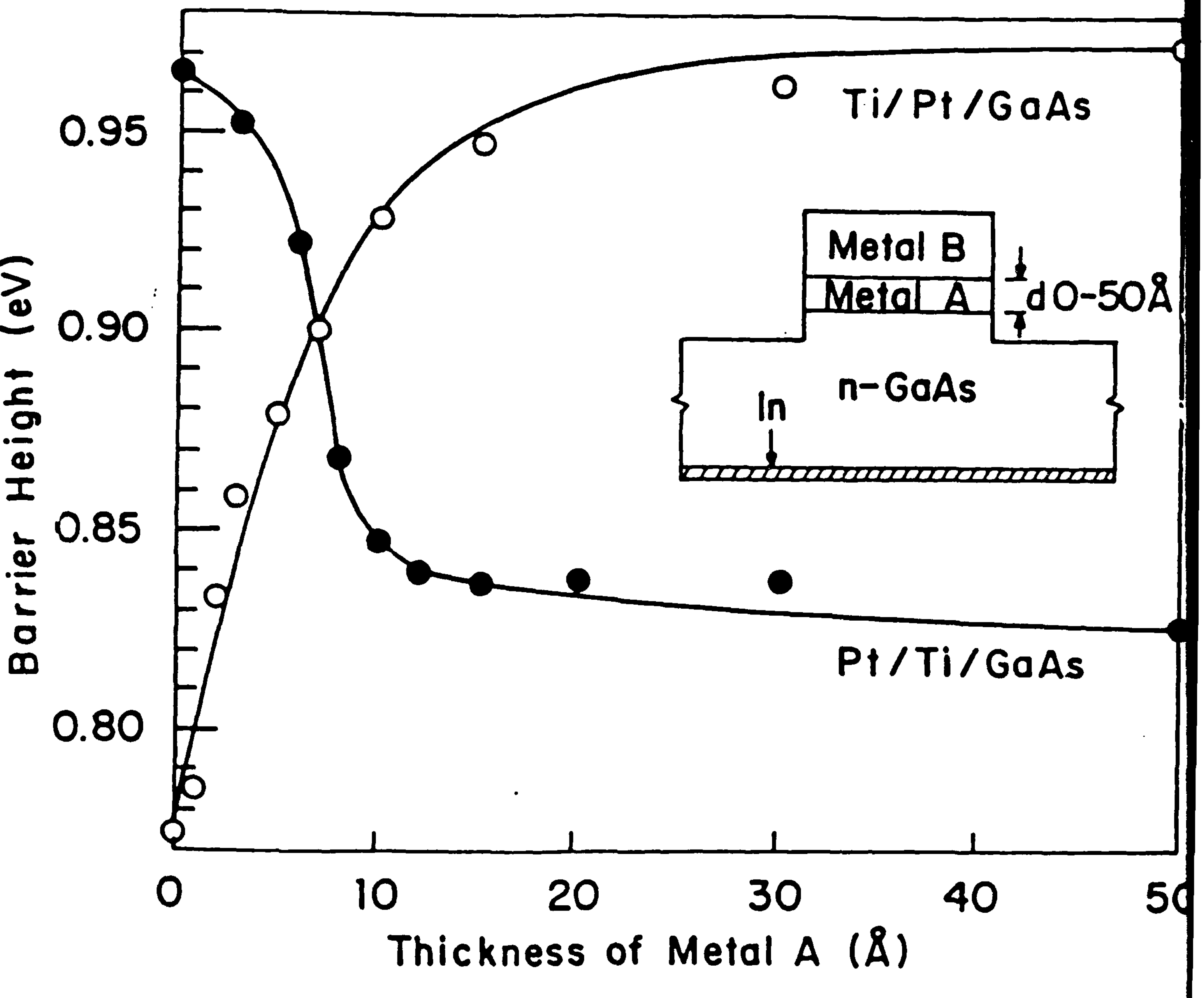

Figure 1. Measured Schottky barrier height as a function of the inner metal thickness for both Pt/Ti/GaAs and Ti/Pt/GaAs bimetal Schottky diodes. The data is for samples annealed at 300C° prior to thick metal deposition. Inset shows the structure of the bimetal Schottky diode, where the thickness of metal A varies from 0 to 50 Å, with 400 Å of metal B for all the diodes.

these diodes were obtained by the I-V method. A Keithley 26000 logarithmic picoammeter which has a current span of eight decades was used in the experiment. An IBM AT computer with an A/D converter was used to generate the bias voltage as well as to collect the data. Before the measurement, all samples underwent a mesa etch by dipping in $NH_4OH:H_2O_2:H_2O$ (20:7:973) for 2 min. This mesa etch has proven very effective in reducing the peripheral leakage current which is crucial for the measurement of high barrier diodes. The results obtained from the 300°C annealed diodes are plotted in Figure 1, where each data point represents an average barrier height of at least three identical diodes. The statistical fluctuation of the barrier height was quite small with a standard deviation of less than 5 mV. For most of the diodes the ideality factor was near 1.05. Only a few exceeded 1.08 and those diodes were simply discarded.

In Figure 1 we clearly see the movement of the Fermi level as a function of Metal A thickness, d. When $d = 0$, the device reduces to the regular Schottky diode. Its barrier height (ϕ_b) is determined by Metal B. For Pt, $\phi_b = 0.97$ eV and for Ti, $\phi_b = 0.77$ eV. It should not be surprising that as the thickness of Metal A increases, the barrier height of the device approaches the Metal A limit. The Pt/Ti/GaAs curve approaching a value of 0.83 eV instead of 0.77 eV is the result of annealing at 300°C. The similar change of barrier height due to annealing was also observed in regular Ti/GaAs diodes. For Pt/GaAs diodes, there is no substantial barrier height difference before and after annealing. However, it is surprising that for both cases, the barrier height transition extended over 10 Å, which is equivalent to 4~5 monolayers of the thin metal. For the Pt/Ti/GaAs diodes without annealing, an even longer transition (~25Å) was observed. At such a thickness the metallic character of the thin film has been well established.[6] According to some theoretical calculations, the metal screening length is typically 0.6 Å.[2,7] In other words, 2~3 Å of Metal A should have completely shielded the effects of Metal B. Nevertheless, our results clearly tell us that is not the case.

Is it possible that when d is small, Metal A does not form a uniform film so that the GaAs substrate in some spots is exposed directly to Metal B? If that happened, the barrier heights measured would actually be the result of two different schottky diodes in parallel. Then, the diode having a lower barrier height would dominate the device I-V characteristics, even though it occupies merely 1% of the total area.[8] This would lower the observed barrier

height values of the Ti/Pt/GaAs samples, but not for the Pt/Ti/GaAs case since the Pt (Metal B) has a much higher barrier height than Ti. However, the data shown here do not seem to bear this out. In some early Ti/Pt/GaAs diodes, we did see the barrier height saturate around 0.92 eV for d>8Å. A closer inspection of the samples found that this was caused by the Ti overlap on the diode periphery. After a careful alignment and an excessive mesa etch, this phenomenon disappeared. In Figure 1, the barrier height of the Ti/Pt/GaAs sample increases rapidly with the Pt thickness, and the variation follows an exponential curve. In contrast, the barrier height decreases rather slowly in the first 6 Å in the Pt/Ti/GaAs case, but afterwards it exhibits an exponential behavior as well. These general trends have been observed in several experimental runs. The small change of the barrier height at the beginning of the Pt/Ti/GaAs curve implies that a strong Fermi level pinning occurs near 0.96 eV (ϕ_b) below the GaAs conduction band edge.[3]

Before this work, several studies showed that the Fermi level at the GaAs surface reaches its final position at a submonolayer metal coverage.[9-12] However, other groups have observed a similar behavior as we report in which the Fermi level evolves over 10 Å of metal coverage.[13,14] All of these experiments were based upon photoemission spectroscopy on the thin metal film. The energy resolution, as well as the depth resolution, is limited for photoemission spectroscopy and the raw data--the core-level shifts--could be obscured by chemical reactions.[15] Our experiment, however, supplies information on this issue from a different approach where the results are, for the first time, based on the direct measurement of the Fermi level shift in fully formed Schottky diodes. As an interface spectroscopy,[3] this method also provides very good energy resolution of mV range. All of these should be valuable to the understanding of Schottky barrier formation.

The authors would like to thank P. Shaw for the assistance of his skillful computer programming. In addition to JSEP, this research was also supported by the Air Force Office of Scientific Research, Contract F30602-85-C-0067, and the Office of Naval Research, Contract N00014-86-K-0694.

2. NEW OPTICAL MATERIALS AND SOURCES

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Research Area II, Work unit 2

The objective of this new JSEP work unit, which began in April of this year, is to understand the optical, electronic, and structural properties of II-VI semiconductor heterostructures and superlattices, using various optical probing and pressure tuning techniques. This research will assist the development of new optical and electronic technologies based on these materials.

The first aim and a major goal in the program is to examine photoluminescence of II-VI epilayers and multiple quantum wells as a function of pressure, using a diamond anvil cell to achieve pressure tuning. We have entered into a collaboration with Professor Robert Gunshor at Purdue University, who leads their II-VI semiconductor MBE program, to obtain samples for study. At present we are examining a 2-mm thick ZnSe epilayer on a GaAs sample which he has supplied to us. Using a closed-cycle refrigerator system cryostat, which we recently obtained through the JSEP program, we have examined the photoluminescence of these epilayers near 4430 Å down to a temperature of 10 K, corroborating similar measurements by the Purdue group. These spectra are shown in Figure 1, taken at 10, 50 and 100 K. Operation at cryogenic temperatures is necessary to do high resolution spectroscopy of these semiconductors, as evident from the sharp exciton features observable only at 10 K in Figure 1. During initial testing of the optical cryostat, we have also examined the photoluminescence of GaAs and fluorescence of ruby, the latter to be used as an in-situ optical probe to measure pressure in the diamond anvil cell, as is shown in Figure 2.

We have obtained a Merril-Bassett diamond anvil cell which is small enough to fit within the radiation shield of the cryostat, and have cooled it to 9 K in the cryostat, at ambient pressure and at modest elevated pressure (10 Kbar). At and above ambient temperatures, the gasketed samples between the diamond anvils are loaded with a methanol/ethanol mixture to ensure that the elevated pressures will be hydrostatic. However, this mixture freezes at cryogenic temperatures and is no longer of use at these low temperatures; instead, for low-temperature operation, cells are loaded

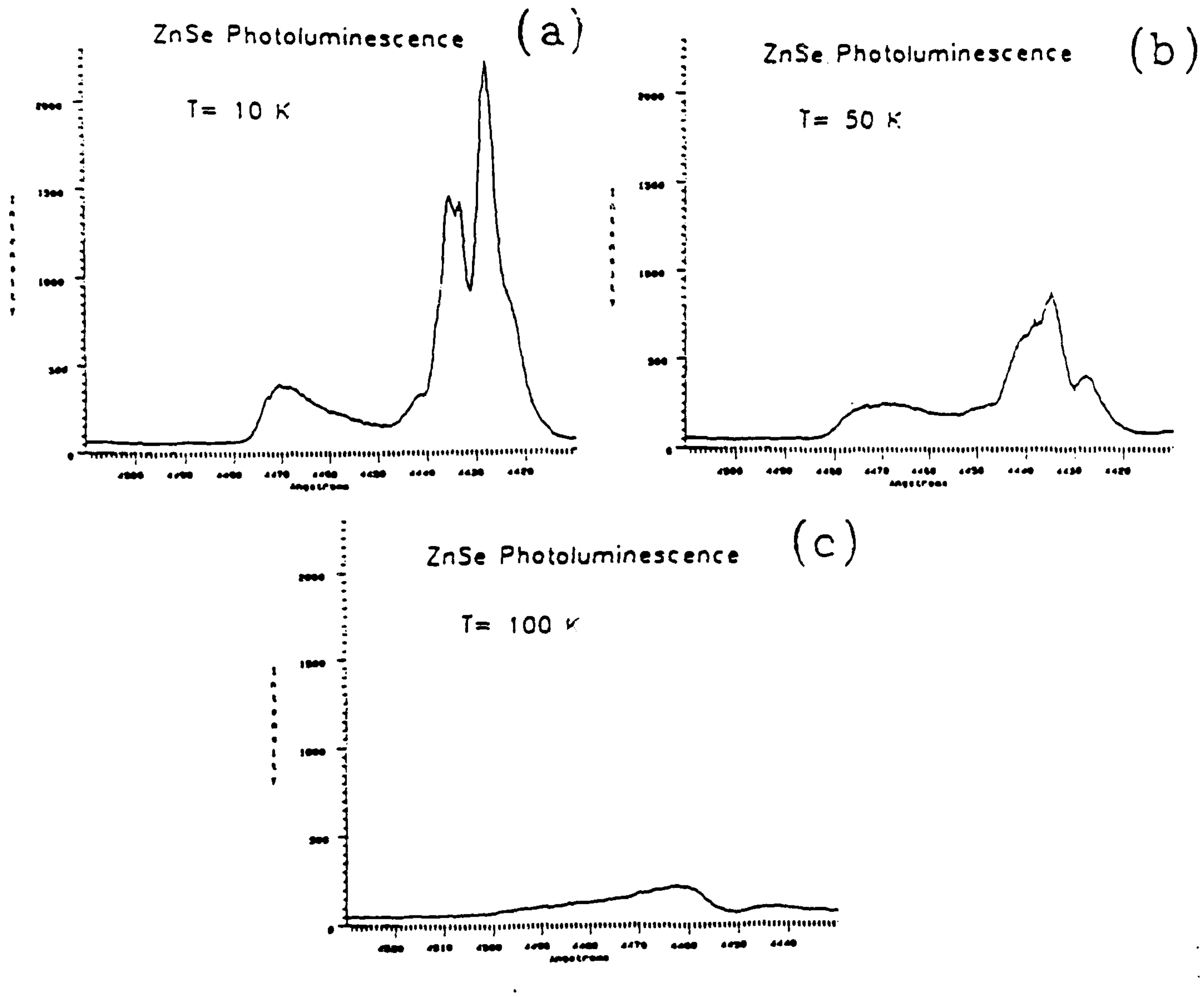

Figure 1. Photoluminescence spectra for ZnSe at (a) 10, (b) 50, and (c) 100 K. The sharp exciton features are observable only at 10 K.

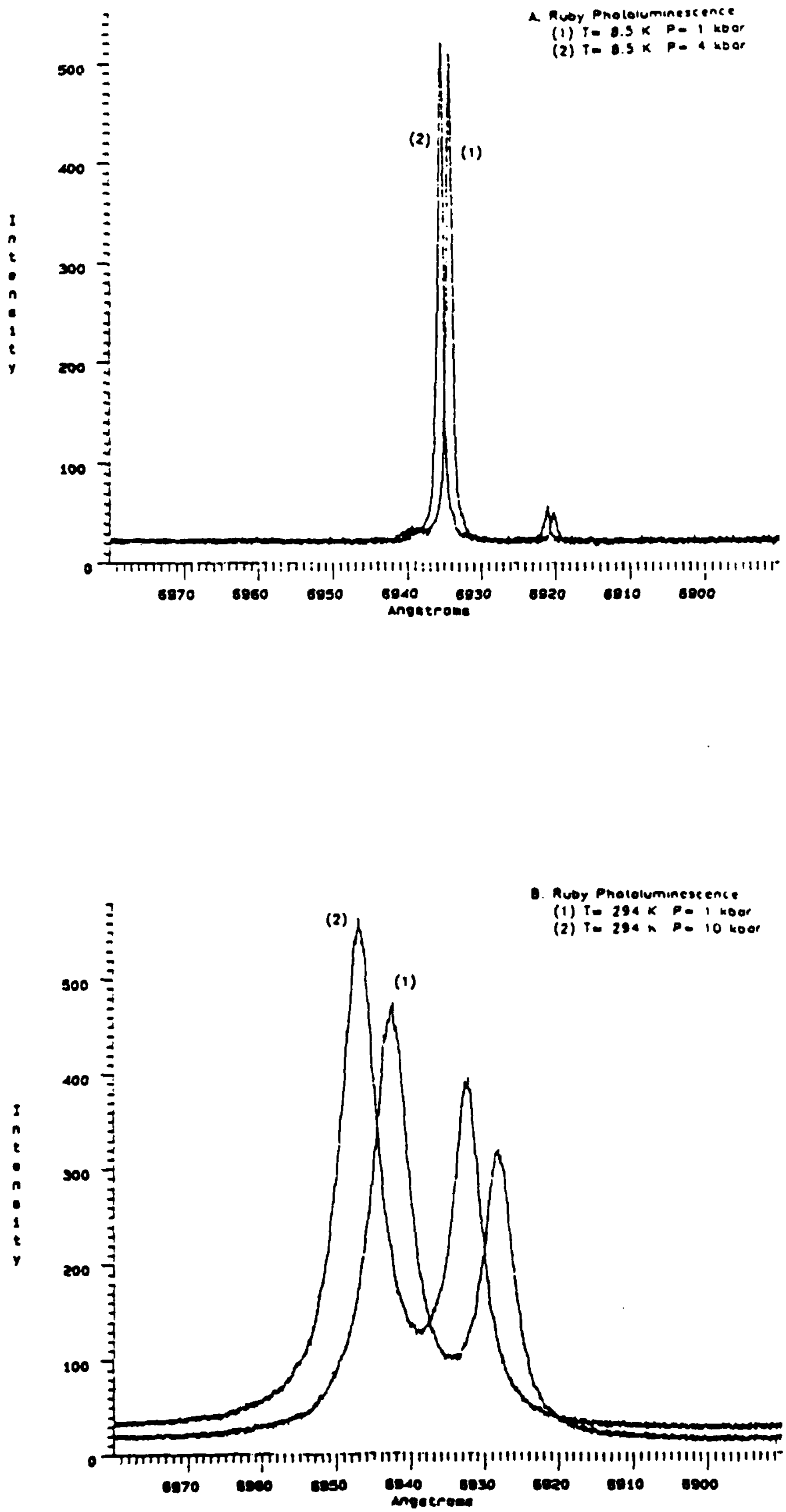

Figure 2. Pressure related shifts in ruby fluorescence, at (a) 8.5 K and (b) ambient temperature 294 K.

with a liquified rare gas. We have set up an apparatus to liquify argon by flowing gaseous argon in tubes cooled by liquid nitrogen, and are just beginning to load diamond anvil cells with liquid argon.

Figure 2 shows the fluorescence of ruby crystals at low temperature (a) 8.5 K and at ambient temperature (b) 294 K, for low and moderate pressures, taken in the Merril-Basset cell. Shifts in these plots are used to determine the pressure in the diamond anvil cell from known calibration curves.

We have also examined several methods of dicing the semiconductor sample into the 100-mm lateral dimension sections needed for loading structures into the gasketed-region of the pressure cells. Care needs to be exercised so that the epilayer is not damaged or removed during dicing. Suitably small samples have been made by potting the front ZnSe surface in wax and back-etching the GaAs wafer by sulfuric acid to a thickness of about 30 mm. The front surface of the sample is then mounted in vaseline, and the back surface is scribed to produce the final samples. The initial thinning of the wafer makes the dicing simpler and also ensures that the wafer will always be thinner than the gasket after installation and pressure tuning (~150 mm).

We have successfully loaded diamond anvil cells with liquid argon and ZnSe epilayer/GaAs samples, and have begun spectroscopic studies in this system. The results of this work will be reported on in the coming period.

In addition to JSEP, this research was also supported by the Office of Naval Research, Contract N00014-86-K-0694.

3. ULTRAVIOLET LASER INDUCED ELECTRON AND ION EMISSION FROM SEMICONDUCTORS

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Research Area II, Work Unit 3

A. USE OF PHOTOEMISSION FOR MICROSCOPIC SURFACE PROBING

(Z. Wu,, R. Scarmozzino, and R. Osgood, Jr.)

Photoemission from semiconductor surfaces has been extensively used to determine the energy levels in semiconductor materials and their bulk material properties such as doping.[1,2] Photoemission from metal conductors in integrated circuits has recently been used as a microscopic probe of circuit performance.[3] We have recently demonstrated the use of photoemission scanning spectroscopy to map the doping and surface properties of semiconductors. In the experiment, a focused UV laser beam is scanned across a patterned semiconductor, and differences in surface properties such as doping are observed as differences in emitted photocurrent. When implemented in a practical system, such a technique can provide an <u>in situ</u> probe of doping levels or doping patterns in a semiconductor wafer.

The experimental apparatus for the demonstration consists of a cryopumped stainless steel vacuum chamber which holds the sample and collector at a pressure of 10^{-8} to 10^{-6} Torr. The collection arrangement is shown in Figure 1. The collector is a stainless steel plate located about 1 mm above the sample, and has a 2 mm aperture to allow illumination by the laser beam. It is biased ≈ 70 V positive relative to the sample in order to aid the collection of the emitted electrons. The voltage drop across a series resistor (10 MΩ) measures the collected current. A lock-in amplifier is used in conjunction with chopping the laser beam (f = 1650 Hz) in order to improve the signal- to-noise ratio. With this arrangement, currents as low as 10^{-13} amps are detectable. The laser wavelength is 257 nm (4.82 eV) and is obtained from an argon-ion laser using an intracavity frequency doubler, which yields power levels up to 40 mW. The laser beam is translated by a set of X-Y stages with 0.1-μm resolution, and is focused by a 16X UV transmitting microscope objective to a spot size of about 1.7 μm (FWHM). The samples used were strongly doped p-type silicon (10^{20} cm^{-3}, 1-0-0 orientation), weakly

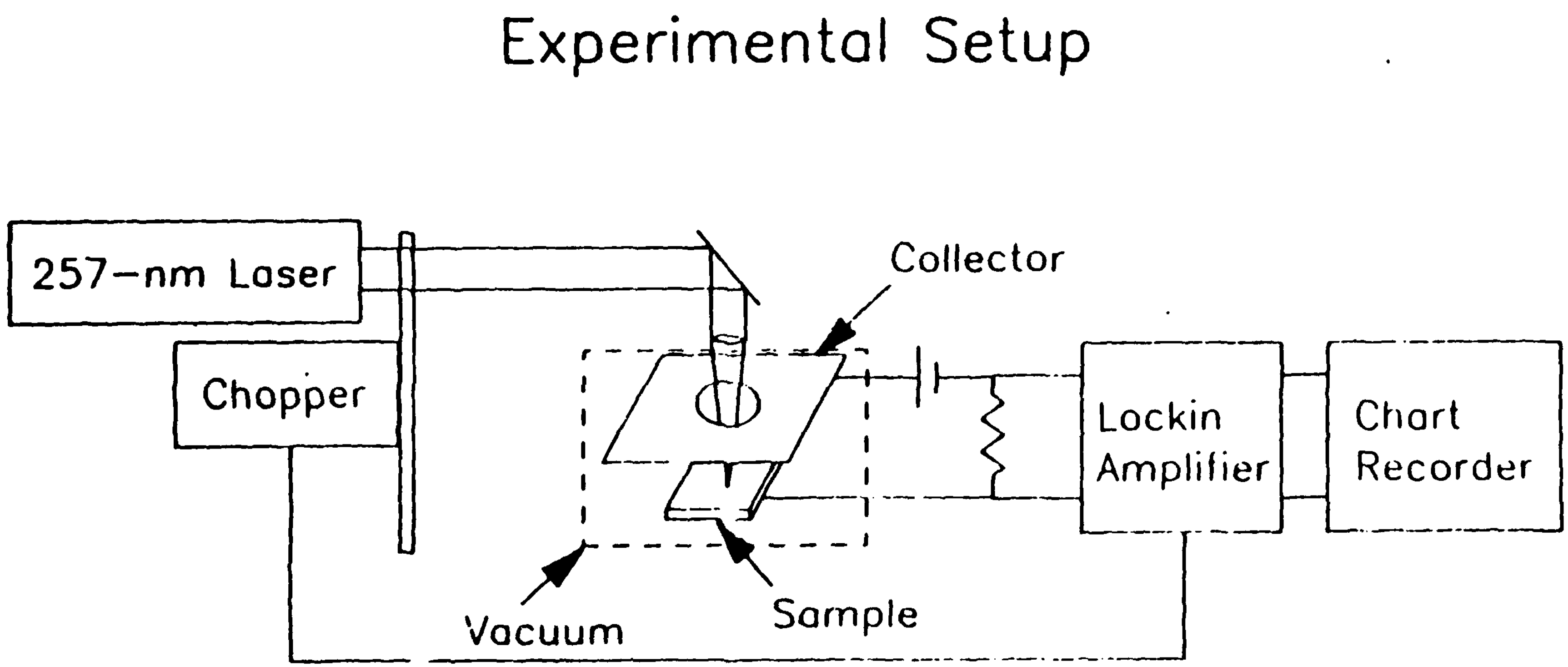


Figure 1. The collection arrangement for the detection of photocurrent.

doped p-type silicon (10^{14} cm^{-3}) patterned with 25 μm lines of p^+ (10^{18} - 10^{19} cm^{-3}) or n^+ (10^{19} - 10^{20} cm^{-3}) regions, and p-type silicon (10^{14} cm^{-3}) patterned with narrow 2-μm wide oxide lines.

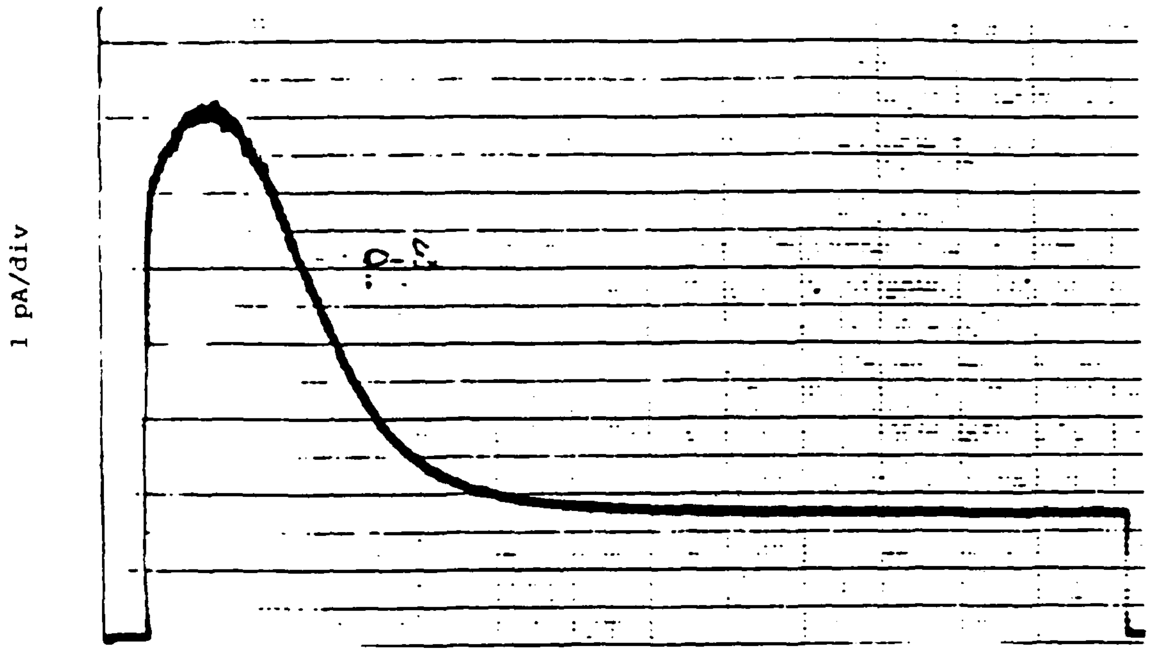
Given that our photon energy of about 4.8 eV is slightly below the photoelectric threshold for silicon, the question arises as to whether multiphoton effects are important. A measurement of photoelectric yield versus laser power exhibited a linear dependence on power, indicating that single photon photoemission is the dominant effect observed in these experiments; the emission most probably originates from a surface states' falling below the bulk conduction band.

A typical trace of the photocurrent versus time for a stationary laser spot on the weakly doped p-type silicon region is shown in Figure 2. Upon steady illumination, a photocurrent is measured which subsequently rises, reaches a maximum, and then decays to a nearly steady state value. We believe this phenomenon to be the result of adsorbed gases, possibly water vapor, which can affect the work function of a surface considerably, and whose surface coverage can be influenced by illumination.[4,5] UV-enhanced oxidation of the surface may also play a role. We plan to further study the chemical physics behind this phenomenon; however, for the purposes of this paper it has not prevented our study of the differences in underlying bulk properties.

Figure 3 shows plots of photocurrent versus time obtained while scanning the beam across the p^+-on-p and n^+-on-p samples. As expected from the results of [2] on the yield versus doping at low photon energies, the signal is found to be higher on the highly doped regions. The measured width of the doped regions is ≈ 26-31 μm and is identical with the patterning width. Note the enhanced signal at the edges of the pattern, an effect which was repeatable over many different patterns. We believe this to be due to the morphology of the surface, in which the highly doped regions have a slightly different elevation than the substrate or simply cause an edge enhancement similar to that observed in micro Raman studies. This may cause other crystal planes to be exposed to the light, leading to a change in the yield. The spatial resolution indicated by Figure 3 was of the order of 2 μm, and corresponds to the laser beam spot size.

In conclusion, we have demonstrated that photoemission induced by a focused UV laser beam can be used as a probe of the material properties of a

P = 5.2 mW



50 sec/div

Figure 2. Photocurrent versus time for stationary illumination.
Sample: weakly doped p-type silicon.

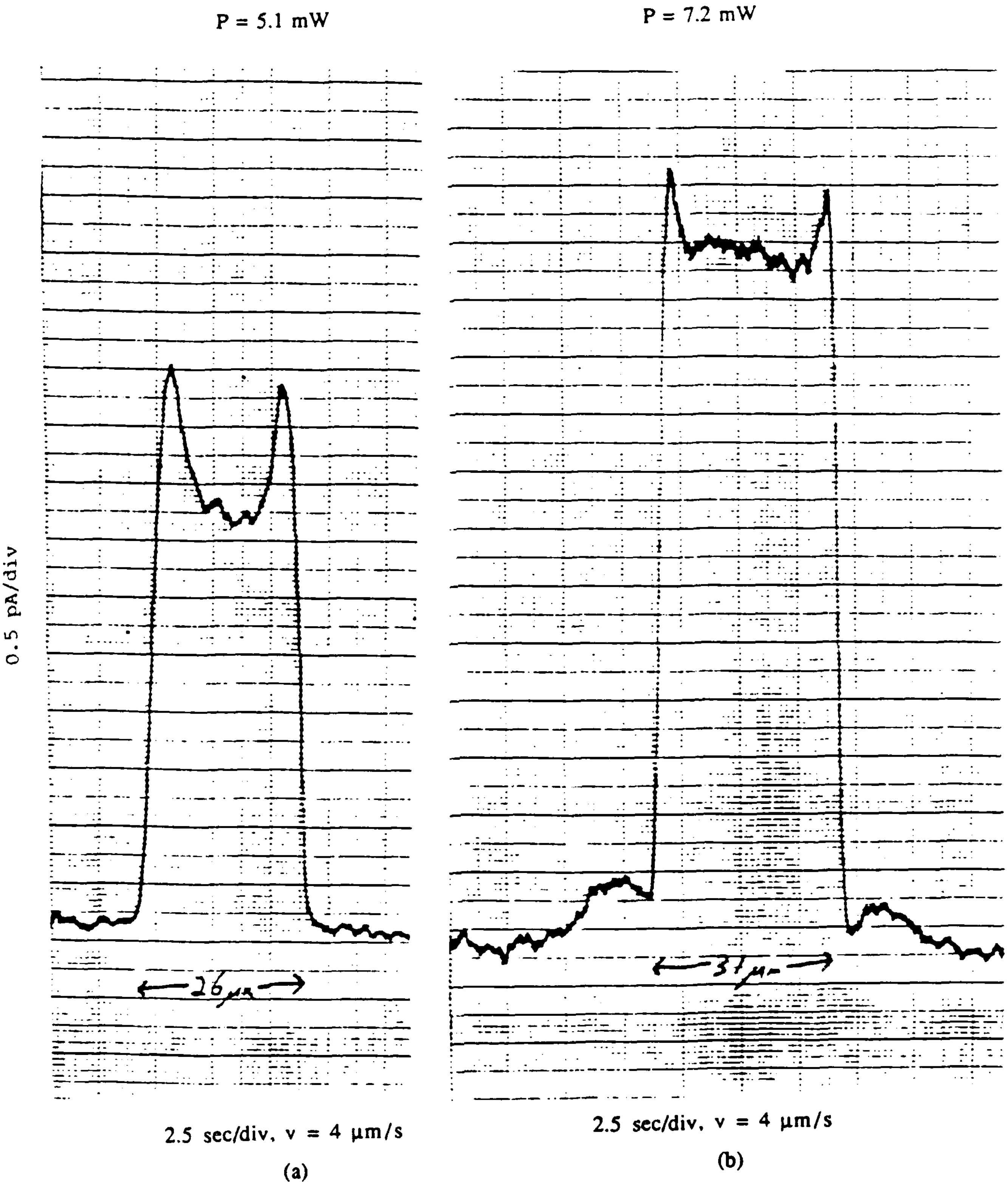


Figure 3. Photocurrent versus time while scanning the laser beam at 4 μm/sec. Samples: (a) p^+-on-p, and (b) n^+-on-p.

semiconductor surface. The spatial resolution of the focused beam was limited only by the laser beam spot size.

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B. ENHANCED PHOTOELECTRON EMISSION FROM UV-IRRADIATED PHOTOCATHODES

(L. Chen, J. O'Neill, V. Liberman, Z. Wu, and R. Osgood, Jr.)

Recently a considerable amount of work has been done developing high current photoelectric injectors for free-electron lasers.[1-3] The design is based on laser irradiated photocathode emitters, allowing for the high beam brightness. The increase in brightness is achieved through maximizing the photocurrent (i.e., >500 amperes/cm^2 from a CsSb photoemitter), and minimizing beam emittence and energy spreading. One of the fundamental limitations of the photocurrents, however, is the generation of space charge.

We report on an approach to remove the space charge limitation through accompanying ejection of positive ions from the photocathode surface. In studying charged particle emission from excimer-irradiated Si surfaces, we have observed that above a certain laser fluence threshold, the emission of photoelectrons is accompanied by the emission of positive ions. The ion emission causes neutralization of the space charge and a more than an order of magnitude increase in the photocurrent. The resulting screening of electron-electron interactions should also significantly improve the beam emittance properties (reduction of the spatial beam spreading). Thus, the concomitant ion emission greatly enhances the overall beam brightness.

The experimental arrangement for charge particle detection is shown in Figure 1. A Si sample (~ 1cm^2) is situated in a vacuum chamber (~ 10^{-6} Torr.). Three excimer laser lines were used to study photoemission -ArF, KrF, and XeF lines with respective energies of 6.4 eV, 5.0 eV, and 4 eV. The excimer laser beam is incident on the sample surface at a 45^{o} angle. The charged particle collector is located normal to the surface at a distance of 14 mm away from the sample. The collector wire, biased either positively or negatively between 90 V and 400 V, is used for detection of photoelectrons or photoions, respectively. The photocurrent pulse is measured with a fast oscilloscope. Angle resolved measurements of the ion velocity with respect to the sample surface were done on a separate time of flight mass spectrometer.

For a typical n-type Si(111) sample (10^{15} cm^{-3}), the dependence of the collected charge on the incident laser fluence is illustrated in Figures 2a and

General Experimental Setup

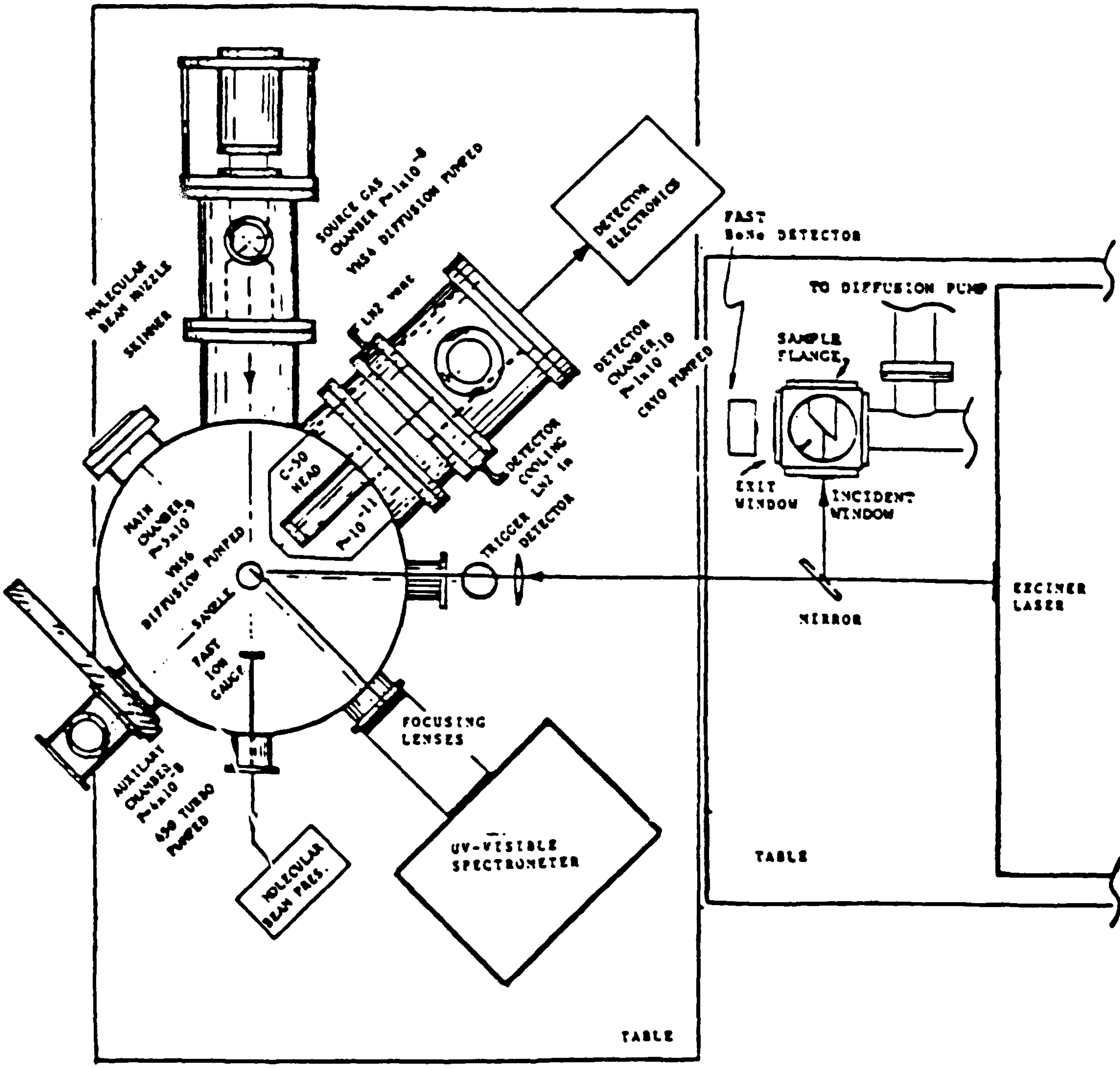

Figure 1. General experimental setup.

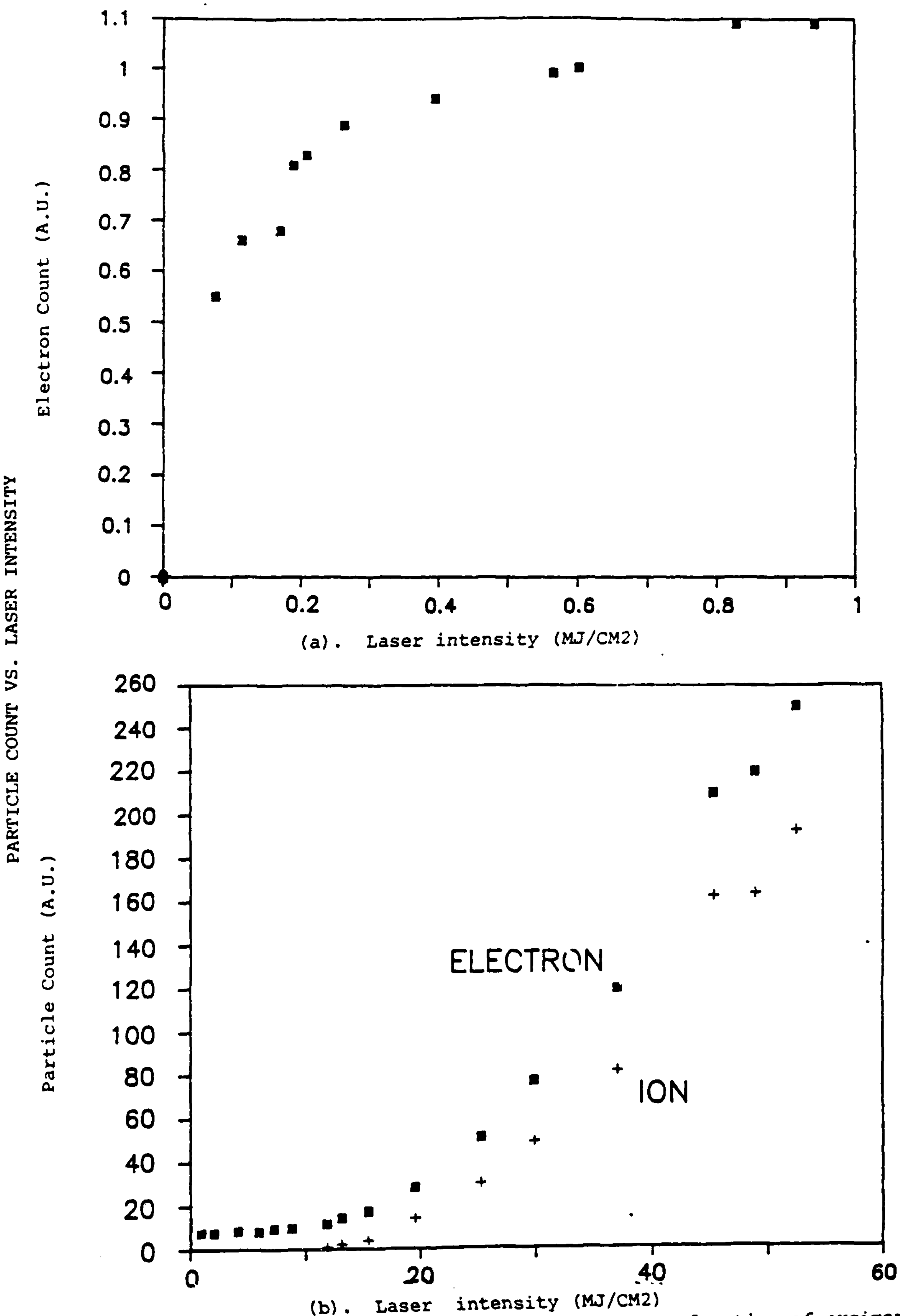

Figure 2. Photoelectron and photoion emission signal as a function of excimer laser intensity at 193 nm from Si.

2b, under conditions of 193 nm irradiation. For this sample, the photoelectron emission increases linearly with laser intensity at the lowest fluences studied (<1 mJ/cm^2). As the incident laser fluence increases, however, the observed photoelectric signal saturates as space-charge screening becomes important. As the laser fluence is increased further (> 12 mJ/cm^2), the photoelectric current increases rapidly with the incident laser fluence. At this point, positive ions are observed to emanate from the substrate. This ion removal process serves to diminish the space charge field and to further enhance the ejection of electrons from the bulk.

Irradiation of the same sample at 248 nm shows similar behavior with the ion-emission threshold occurring at 36 mJ/cm^2. While the ion emission threshold observed in these experiments is sensitive to surface roughness, it is consistently lower for 193-nm than for 248-nm illumination, and in all cases it is an order of magnitude below the laser fluence necessary to cause the Si substrate to melt. Measurements were also performed at 351 nm, but no emitted electrons or ions were observed for low laser fluences employed in these experiments (<100 mJ/cm^2).

The wavelength dependence observed here is consistent with the known behavior of the photoelectron emission cross section for silicon, that is 6.4 eV (193nm) is well above the photoemission threshhold for silicon, while 351 nm (4 eV) is well below it. The mechanism for the ion emission is not known at this time, except that it is clearly a nonthermal effect associated to some degree with surface damage.

In order to estimate the enhancement in photoemission that would be obtainable by eliminating the space charge effect, we give a brief discussion of space charge effect. The space charge limited current in the cw case is given by the Child-Langmuir equation:[4]

$$I_{cw} = \sqrt{\frac{2}{9\pi}}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{a^2} \tag{1}$$

where -e is the electron charge, m its mass, V the bias voltage, and a the distance between the anode and the cathode. Eq. (1) can also be written as

$$I_{cw} = 2.33 \times 10^{-6} \frac{V^{3/2}}{a^2} \text{ A/cm}^2$$

where V is in units of volt and a in cm.

Now if the ions are simultaneously emitted with the electrons, space charge is eliminated and the current is thus given by:

$$I_{pulse} = \frac{\eta P e}{h\nu} \tag{2}$$

where P is the incident laser power, η is the cathode efficiency, and $h\nu$ is the photon energy.

When ion emission occurs, much higher currents are obtained. In the experiment reported here, the laser photon energy (6.4 eV) is well above the threshold for photoemission, and consequently $\eta \approx 10^{-3}$. In this case, the advantage gained in limiting space charge is considerable. In fact, with complete neutralization, the increase in photocurrent is expected to be more than four orders of magnitude.

In summary, we have suggested an approach to overcoming the fundamental limit in the photocurrent due to space charge. Illumination of Si photocathodes with deep UV excimer laser radiation results in concomitant emission of positive ions and elimination of the photoelectron space charge. In addition to increase in photocurrent, this technique improves beam emittance by reducing electron-electron interactions. The lower laser fluences needed to eliminate the space charge effect suggest that the photocathode damage would be minimal.

In addition to JSEP this work was supported by the IBM Corporation.

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C STUDIES OF THE SURFACE PHOTOCHEMISTRY OF DIMETHYL-CADMIUM ON SILICON USING INFRARED INTERNAL REFLECTION SPECTROSCOPY (J. O'Neill and R. Osgood, Jr.)

Laser driven photochemical processes on surfaces have been the focus of much recent theoretical and experimental investigation.[1] In the field of microelectronics, much of this attention has addressed the surface photochemistry of metal alkyls because of their importance in laser chemical vapor deposition of thin metal films.[2,3] While the practical implications of such photoinitiated surface reactions are well appreciated, many questions remain concerning the fundamental aspects of the interaction of laser radiation with surface adsorbates. Underlying any understanding of such photoinitiated surface processes is the need to characterize the chemical nature of adsorbed precursor molecules at the gas-solid interface. A variety of spectroscopic techniques have been developed which are capable of monitoring the chemical behavior of surface adsorbates.[3-5] Among these, infrared spectroscopic methods have been particularly useful in elucidating the structure of a number of molecules on metal, semiconductor and insulator substrates.[4-8]

Recent experiments in our laboratory used an infrared spectroscopic technique to monitor the infrared absorption spectra of weakly bound physisorbed molecules at the interface of a gas-solid system.[9,10] This technique, which has been described in detail previously, employs the principle of total internal reflection (TIR) to isolate the absorption signal due to surface molecules from that due to ambient gas-phase species.[10,11] Briefly, Fourier-transformed infrared radiation focused on one end of an IR transparent internal reflection element located in a stainless steel vacuum cell. The probe beam experiences approximately 50 reflections as it propagates through the element. An evanescent field, which penetrates beyond the solid-gas interface at each reflection point, is capable of interacting with molecules adsorbed at this boundary giving rise to the measured absorption spectra.[11] The enhanced sensitivity which is gained by these multiple reflections readily allows for the detection of a variety of adsorbed species at submonolayer coverages.

The present work examines the photochemical behavior of both chemically and physically adsorbed dimethylcadmium species upon exposure

to excimer laser radiation at 193 and 248 nm. By monitoring changes in the infrared spectra of adsorbed dimethylcadmium during the irradiation process, insight into the role of the surface in the photodissociation process of the surface species is obtained.

The polished silicon internal reflection element used in these experiments was chemically degreased using a standard microelectronic device cleaning procedure.[12] Prior to mounting in the vacuum cell, the element was subject to successive treatments with H_2SO_4/H_2O_2 (1:1) and HF (10%) solution. For experiments on oxidized silicon, the final treatment was with H_2SO_4/H_2O_2, while hydrogen "passivated" surfaces were prepared upon treatment with dilute HF solution. Such passivated surfaces are hydrophobic and have been characterized as unreactive for extended periods of time (up to 1 hour under atmospheric conditions) due to the presence of hydrogen atoms at each silicon dangling bond site at the surface.[13,14] The sample element is baked in vacuum at temperatures of approximately 125-150o C for several hours in order to remove adsorbed water from the surface.

Fourier transformed infrared spectra of adsorbed DMCd were recorded in the region from 2-5 μm where absorption bands corresponding to CH stretching vibrations of the methyl ligands occur for the gas-phase molecule.[15] Typical absorption spectra for physisorbed and chemisorbed dimethylcadmium present on both oxidized and passivated silicon surfaces are presented in Figure 1. The physisorption spectra were obtained in the presence of 30 Torr of ambient DMCd gas, while the chemisorption traces were observed upon subsequent evacuation of the sample cell to a pressure of $\sim 1 \times 10^{-8}$ Torr. The marked enhancement in adsorption of the organometallic species on oxidized silicon has been attributed to the presence of a monolayer of silanol (Si-OH) groups which are known to occur on such oxides.[10,16] No detectible chemisorption and little physisorption is observed on silicon surfaces prepared under conditions where rigorous hydrogen passivation is maintained. Previous work carried out on this system employing XPS surface analysis techniques indicate that this strongly bound layer on Si/SiO_2 surfaces is due to the binding of a dimethylcadmium adspecies.[17,18]

Experiments were performed to examine the behavior of the chemically adsorbed layer formed on Si/SiO_2 surfaces upon UV irradiation at 193 and 248 nm. In these studies, approximately 60% of one side of a DMCd-dosed internal-reflection element (30% of the total surface area) was

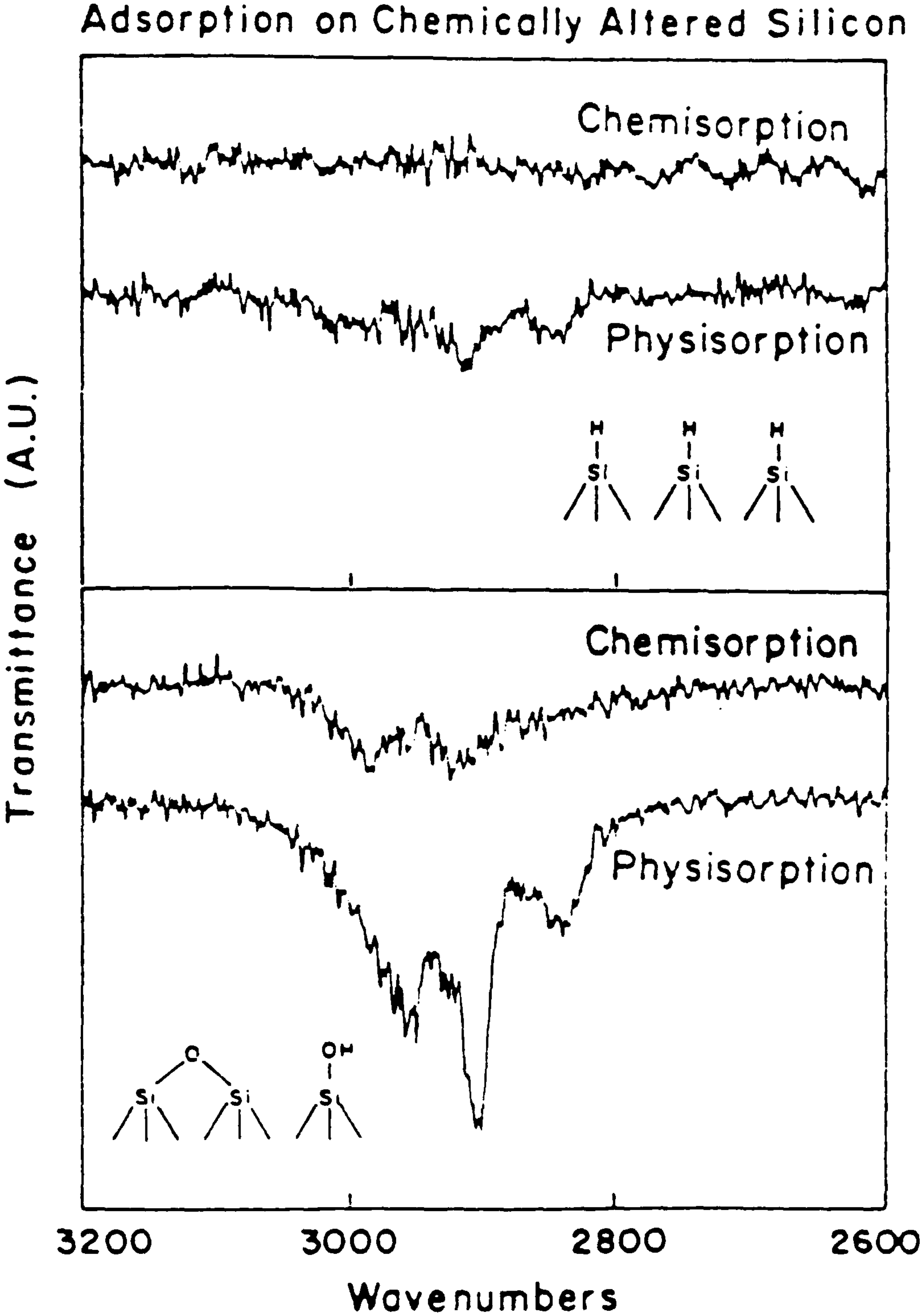

Figure 1. Typical FTIR absorption spectra for chemically and physically adsorbed dimethylcadmium on a) hydrogen passivated silicon and b) oxidized silicon surfaces. The physisorption traces observed in the presence of 30 Torr. of ambient DMCd, while the chemisorption signals were obtained after subsequent evacuation of the cell to pressures of 1×10^{-8} Torr. Note that adsorption is enhanced on oxidized silicon due to the presence of -OH groups known to occur on these surfaces.

illuminated with pulses from an excimer laser operating at 2 Hz. Figure 2 illustrates that upon irradiation at 193 nm, the intensities of the observed IR absorption features decrease to 70% of their original value. (I=3.8 mJ/cm^2, T_{irrad}=1.5 min.) On the other hand, illumination of the silicon element with higher intensity 248 nm light (15.3 mJ/cm^2) for extended periods of time (10 min.) causes no observable change in the chemisorption spectrum. While the relative UV absorption cross-section for the chemisorbed surface species is approximately 4-5 times smaller at 248 than at 193 nm,[16] the total photon flux incident on the surface is 35 times larger at 248 nm. Therefore, the observed differences in photochemical behavior at these two wavelengths cannot be attributed to absorption differences alone.

The decrease in the chemisorption absorption signal observed at 193 nm corresponds to the photoinduced removal of CH containing species from the surface. Thermal desorption effects are expected to be negligible since the maximum surface temperature rise during the laser pulse is less than 10^o at the laser fluences used in these studies.[19] Also, separate TPD studies carried out in our laboratory indicate that desorption does not occur in the DMZn/SiO_2 system at surface temperatures less than 120^o C.

From the present experimental results at 193 nm, an estimate of the cross-section for photoremoval of methyl containing species from the surface can be determined. The change in number density of the chemisorbed molecular layer due to photoinduced processes on the surface can be expressed as:

$$dN/dt = -\sigma N(t)\, n$$

where N(ts) is the number density of chemisorbed molecules at a given time, σ is their photoremoval cross-section and n is the flux of incident UV-laser photons. Solving this equation yields:

$$N(t) = N_o \exp(-\sigma n t)$$

where N_o is the initial number of chemisorbed molecules on the surface. Assuming that all chemisorbed species are removed from the surface under the area illuminated by the laser, the absorption intensity due to chemisorbed molecules drops to 1/e of its original value after approximately 40 seconds of irradiation. (I=3.8 mJ/cm^2 per pulse, rep rate=2Hz, hv=6.4eV/photon, total photon flux=2.8x10^{17} photons/cm^2) From this a cross-section of roughly 4x10^{-2}A^2 is obtained for removal of chemisorbed molecules from the surface by the incident laser photons. Separate

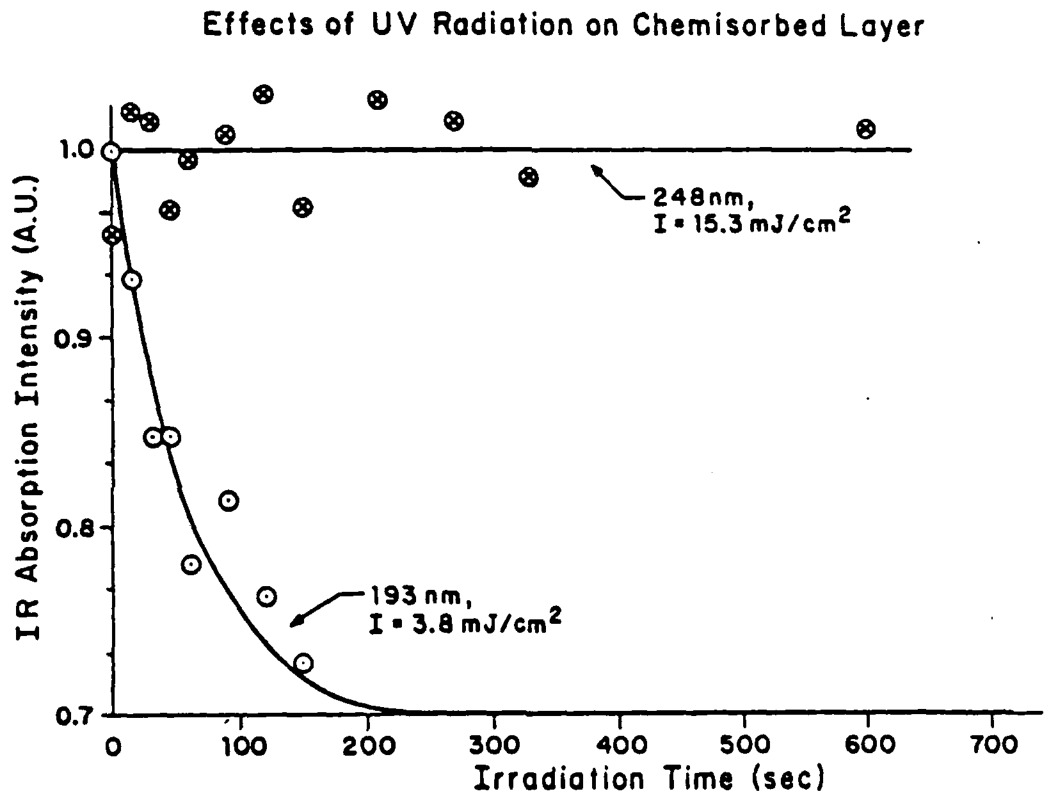

Figure 2. Plot of the infrared absorption intensity for chemisorbed DMCd on oxidized silicon as a function of irradiation time for excimer laser illumination at 193 and 248 nm. Irradiation at 193 nm causes attenuation of the IR absorption signal due to photoremoval of chemisorbed molecules under the area illuminated by the laser. No change is observed for irradiation at 248 nm.

experiments in our laboratory indicate that the total ultraviolet cross-section for chemisorbed dimethylzinc on quartz is similar to the corresponding value in the gas-phase.[16] It is reasonable to assume similar behavior for the dimethylcadmium adspecies on Si/SiO_2. A comparison of the photoremoval cross-section determined in these experiments with the absorption cross-section at 193 nm for dimethylcadmium in the gas-phase (0.2 A^2) suggests that an efficient quenching mechanism is operable on the surface which greatly reduces the photoremoval yield. Such rapid absorbate quenching has been reported for a variety of species on metal surfaces but is unexpected for insulating surfaces.[20,21]

Experiments were also carried out to examine the nature of the thin cadmium film formed on chemically altered silicon surfaces upon UV-laser irradiation of a small physisorbed molecular layer. Such studies were motivated by the desire to understand the fundamental photochemical mechanisms operating under conditions appropriate for laser chemical vapor deposition. In these studies, the infrared CH absorption features due to surface adspecies on both oxidized and hydrogen passivated silicon surfaces were monitored while irradiating the surface at various excimer laser wavelengths in the presence of a small amount of gas-phase dimethylcadmium. The results of one such experiment are illustrated in Figure 3 for the 193 nm irradiation of a Si/SiO_2 surface in the presence of 0.2 Torr DMCd. (I=6.7 mJ/cm^2, rep rate=2 Hz, tirrad=270 sec) Under these conditions, an observable metallic cadmium film is formed on the surface. Accompanying this film growth is an increase in absorption in the CH stretching region of the spectrum. This observation is consistent with the incorporation of CH containing species in the deposited metal film itself. Previous surface analyses using XPS and AES spectroscopic probes were carried out on similar laser-deposited metal layers.[22,23] In agreement with the present experimental results, these studies revealed a high degree of carbon incorporation in these types of metal films. While the precise chemical nature of the species responsible for the enhanced infrared absorption observed in these experiments is not known, the qualitative spectral appearance of the absorption bands, along with their measured frequency positions, suggest that this hydrocarbon content is in the form of methyl containing species.[15,24]

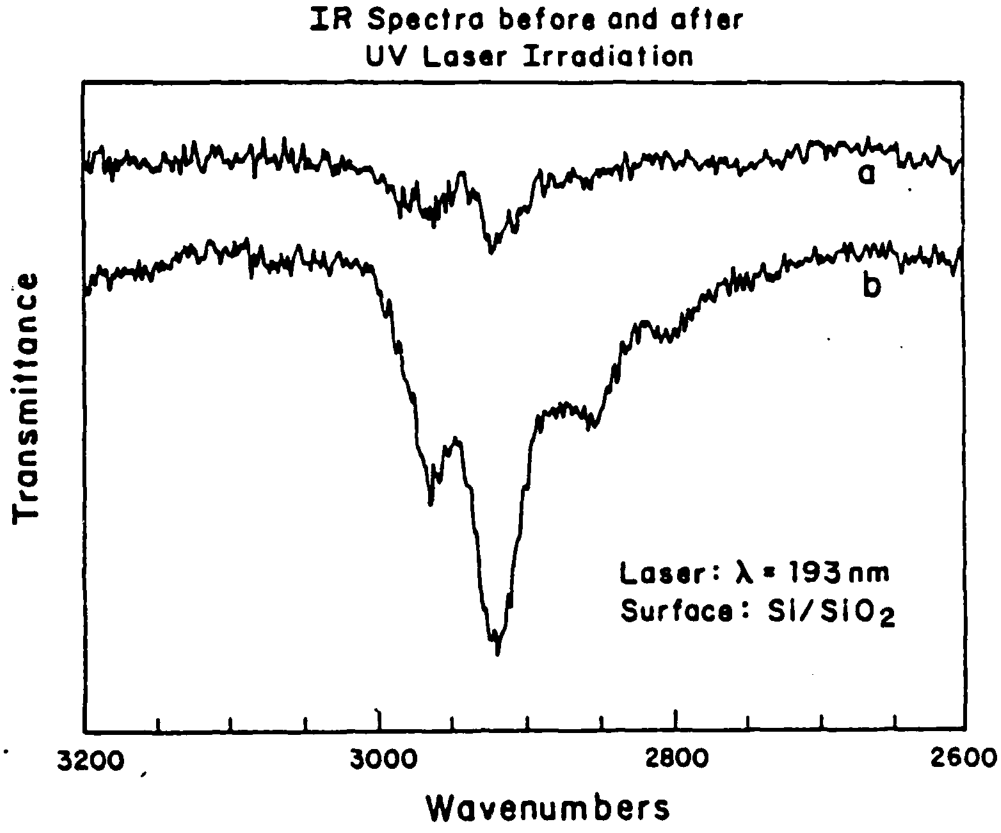

Figure 3. Spectral scan in CH stretching region of spectrum a) before irradiation (corresponding to pure chemisorbed molecular layer) and b) after illumination at 193 nm of a SiO_2 surface in the presence of 0.2 Torr. DMCd. The increase in IR intensity indicates a high hydrocarbon content in the laser deposited metal film. Note the appearance of an additional spectral feature at 2800 cm^{-3}.

Figure 4 illustrates this growth in CH absorption intensity for irradiation of both Si/SiO_2 and SiH surfaces at 248 nm. The increase in absorption intensity is greater in the Si/SiO_2 system than it is on hydrogen passivated surfaces. Qualitatively, separate observations reveal that metal film growth also occurs more slowly on SiH surfaces. These observations are consistent with the enhanced adsorption of the precursor DMCd molecule on oxidized silicon. Such enhancement is illustrated by the relative chemisorption signal intensities on SiH and SiO_2 (represented by the points at t=0 in Figure 4). They also suggest that the nucleation process ultimately responsible for metal film growth is mediated by the ability of the gas-phase precursor to adsorb on the substrate.

In addition to JSEP this research was also supported by the Army Research Office, Contract DAAG29-85-K-0210, and the IBM Corporation.

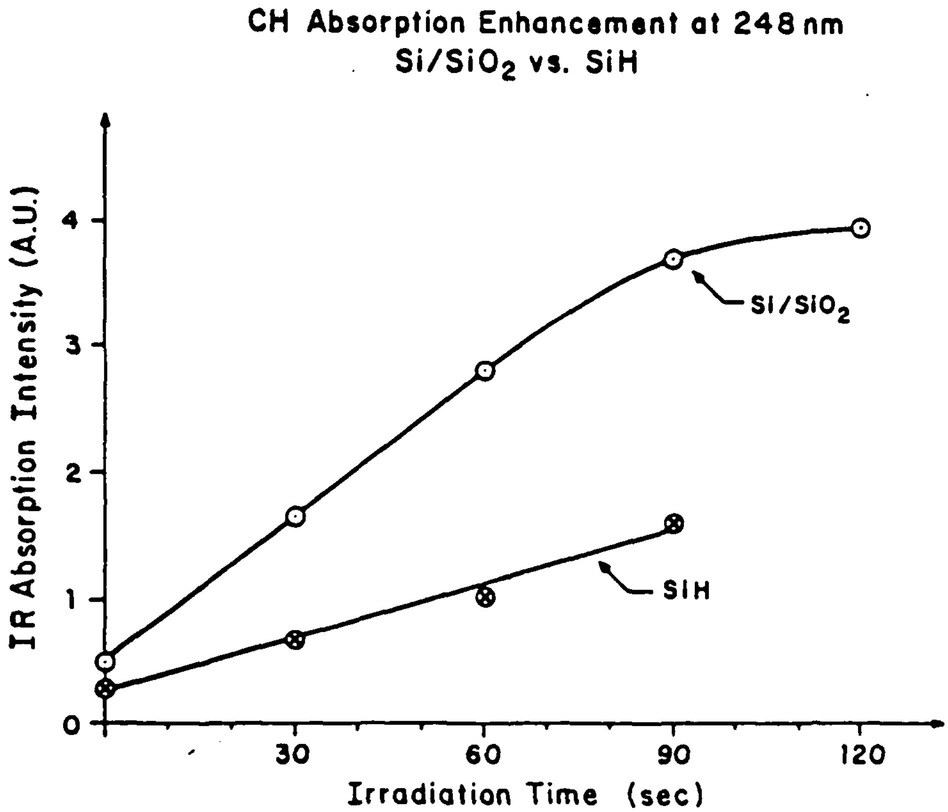

Figure 4. Plot of growth of CH absorption signal as a function of irradiation time at 248 nm on SiO_2 and SiH surfaces. The slower growth on passivated surfaces coincides with an observation that metal film growth is also slower on hydrogen covered substrates.

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4. GENERATION AND DYNAMIC PROPERTIES OF METASTABLE SPECIES FOR QUANTUM ELECTRONICS AND LASER MICROPROCESSING

George W. Flynn, Principal Investigator (212) 280-4162
Work Area II, Work Unit 4

A. DIODE LASER PROBING OF THE ASYMMETRIC STRETCHING STATE OF CO_2 PRODUCED BY QUENCHING OF THE IODINE ION-PAIR STATE $I_2(D)$ (A. S. Hewitt, L. Zhu and G. W. Flynn)

The spectroscopy and dynamics of the low lying electronically excited states (i.e., the valence states) of molecular iodine have been studied in considerable detail for many years.[1-6] In contrast, only in the last few years has the spectroscopy of the ion-pair states of I_2 been unraveled.[7-11] Moreover, few studies of the physical and chemical quenching of these states have been performed.[11-15] To our knowledge, there have been no studies of the quencher states directly populated by the quenching of the iodine ion-pair states.

In this report, we describe the first state-resolved studies of CO_2 quenching of the iodine ion-pair state $I_2(D)$. At 193 nm, iodine absorbs very strongly, mainly to the v=149 level of the D state.[10] At the low pressures used in this experiment, the $I_2(D)$ fluoresces back to the ground state and to a shallow a' state in ~15.5 ns[16] unless it is quenched by CO_2. Time-resolved diode laser absorption spectroscopy has been employed to determine the rotational distribution, linewidths, and absolute cross section for excitation of the $CO_2(00^01)$ asymmetric stretching state.

The experimental apparatus was described in detail previously,[17] and only a brief summary will be given here. 193 nm pulses from an ArF excimer laser with unstable resonator optics were propagated down a 9 foot sample cell which contains a 1/10 mixture of I_2/CO_2 at a total pressure of 27.5 mtorr. Tunable cw radiation from a diode laser at ~4.3 μm was collinearly propagated through the cell with the excimer beam. The diode laser was tuned to various rotational lines in the P branch of the $00^01 \rightarrow 00^02$ vibrational band of CO_2. Time-resolved changes in the transmitted IR intensity were measured with an InSb detector. The signals were digitized and averaged on a digital oscilloscope and sent to a personal computer for storage and later analysis.

The diode laser modulation, excimer laser firing sequence, and data aquisition were controlled by the PC.

For transient linewidth measurements,[18] the diode laser was modulated at 250 Hz over several linewidths of a specific CO_2 absorption line. The Doppler lineshape was determined by firing the excimer laser at different delay times with respect to the start of the modulation cycle. A Fabry-Perot etalon with a free spectral range of 0.0097 cm^{-1} was used for frequency calibration.

A typical time-resolved signal (see inset of Fig. 1) has a detector-limited (~700 ns) fast rise due to the direct formation of excited $CO_2(00^01)$ molecules during the $I_2(D)/CO_2$ quenching interaction. The slower decay arises from diffusion of the excited CO_2 molecules out of the diode laser beam path. To obtain the relative nascent rotational distribution of the 00^01 state of CO_2 shown in Figure 1, the fast rise amplitudes were extrapolated back to t=0 and normalized by the excimer and diode laser powers. It is clear from Fig. 1 that an approximately room temperature Boltzmann distribution fits the observed rotational distribution well.

The nascent transient linewidths of several $CO_2(00^01,J) \rightarrow CO_2(00^02,J-1)$ transitions were measured following excitation by $I_2(D)$. The observed linewidths correspond to room temperature Doppler linewidths.

Preliminary results suggest that the absolute E-V cross section for the excitation of $CO_2(00^01)$ is larger than gas kinetic, implying that long range forces are important in mediating the $I_2(D)/CO_2$ energy transfer process. Since the $I_2(D)$ molecule is really a large oscillating dipole, it is likely that the excitation cross section is due to a dipole-dipole long range force mechanism.

In addition, the population of various $CO_2(00^02)$ levels was measured relative to the population of $CO_2(00^01)$. It was found that $\pi\sigma^2_{002}/\pi\sigma^2_{001}<0.003$. This lends further support to the idea of long range energy transfer mediated by transition dipoles, since the 00^00 to 00^02 transition is not dipole allowed in first order.

It is reasonable to ask if these large cross sections are really due to CO_2 quenching of the intially excited $I_2(D,v{\sim}149)$ molecules. There are three possible alternative excitation mechanisms:

$I_2(D) + CO_2(000,J') \rightarrow I_2^{\dagger} + CO_2(001,J)$: $CO_2(001)$ Rotational Distribution vs. a T=316K Boltzmann Distribution

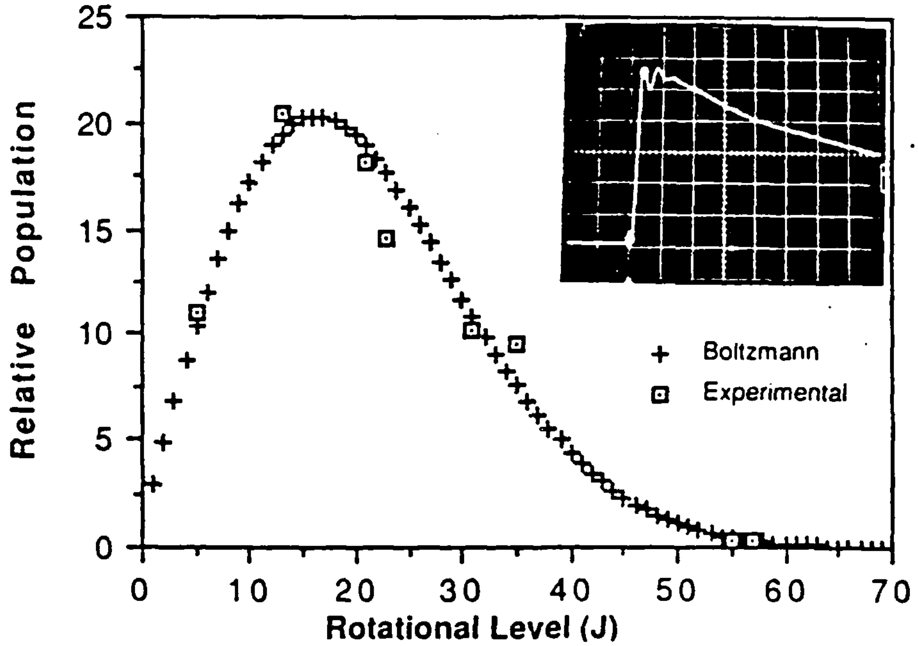

Figure 1. The relative nascent rotational distribution of the 00^01 state of CO_2.

1) Approximately 90% of the initially excited iodine molecules undergo a radiative transition to the ground state or to the low-lying, shallow $I_2(a')$ state,[19] producing 0-1 eV translationally hot iodine atoms and ground state I_2 molecules with a range of vibrational energies which are peaked at v=0. Using a breathing sphere model (SSH theory) it can be shown that the 0-1 eV iodine atoms are not moving fast enough to cause vibrational excitation of the high frequency asymmetric stretching mode (ω=2349 cm^{-1}). Furthermore, it is unlikely that low levels of vibrational excitation of I_2 in the ground state (ω=214.5 cm^{-1}) would be so efficient at exciting $CO_2(00^01)$. In addition, no ground or valence states of I_2 are known to have quenching cross sections greater than gas kinetic.

2) Other ion-pair states of I_2 may contribute to the large excitation cross section. However, all the ion-pair states have nanosecond fluorescence lifetimes which means that of the 10% or less of I_2(D) molecules that undergo a quenching interaction only 10% will undergo a second quenching interaction before fluorescence occurs. Consequently, if the $CO_2(00^01)$ excitation is due to other ion-pair states the cross sections would have to be unreasonably large.

3) The large cross sections may be due to the I_2^+ ion produced by photoionization of I_2(D) when a second 193 nm photon is absorbed.[20] At this point, I_2^+ cannot be ruled out as a possible source of excitation. Excimer laser power dependence studies and ion current measurements will be performed to resolve this issue.

In summary, the $CO_2(00^01)$ nascent rotational and translational temperatures following I_2(D) quenching were about 300 K, implying that approximately 2349 cm^{-1} of energy is transferred resonantly from I_2(D, v~149) to the asymmetric stretching mode of CO_2. The cross section for excitation of $CO_2(00^01)$ was found to be larger than gas kinetic. The excitation mechanism appears to be a long range dipole-dipole interaction.

This research was also supported by the Department of Energy, Contract DE-FG02-88-ER-13937, the National Science Foundation, Grant CHE-85-17460, and the IBM Materials Research Award.

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B. CHLORINE ATOM REACTION DYNAMICS

(J. M. Hossenlopp, J. F. Hershberger, and G. W. Flynn)

1. Introduction--Understanding the reaction dynamics of chlorine atoms is important for both surface and gas-phase chemistry. Chlorine atoms and molecules have been shown to be effective etchants of surfaces, such as aluminum and copper, in both thermal[1,2] and laser-assisted[3] etching studies. The gas-phase reactions of chlorine atoms are of practical importance for the modeling of atmospheric chemistry and for developing chemical lasers. The fundamental questions in surface and gas-phase reactions involve determining the reaction rates and characterizing the reaction products. We have been successful in utilizing time-resolved infrared absorption techniques, using tunable diode lasers, to begin examining chlorine atom reaction dynamics from two perspectives. The gas-phase concentration of chlorine atoms is directly monitored in one set of experiments. The other approach involves probing reaction products, enabling us to determine the rate of reaction and the energy disposal in the products.

2. Results

a. Detection of Chlorine Atoms--The experimental approach to the direct detection of chlorine atoms involves generating the atoms in-situ with a pulsed laser and monitoring the time-resolved changes in absorption of a continuous wave diode laser probe beam which is tuned to the atomic spin-orbit transition. The photolysis and probe beams are copropagated down a 3 meter absorption cell. The general scheme is shown below.

$$Cl_2 + h\nu \ (340 \text{ nm}) \rightarrow 2 \ Cl \ (^2P_{3/2}) \qquad (1)$$

$$Cl \ (^2P_{3/2}) + h\nu \ (11.3 \ \mu m) \rightarrow Cl \ (^2P_{1/2}) \qquad (2)$$

Use of this technique allows the gas-phase concentration of chlorine atoms to be followed in real-time. Figure 1 shows our first results in monitoring chlorine atoms by infrared absorption. The chlorine atoms were generated as shown in (1) in a nonreactive mixture of Cl_2 and argon. The initial signal is proportional to the number of chlorine atoms which are formed in the

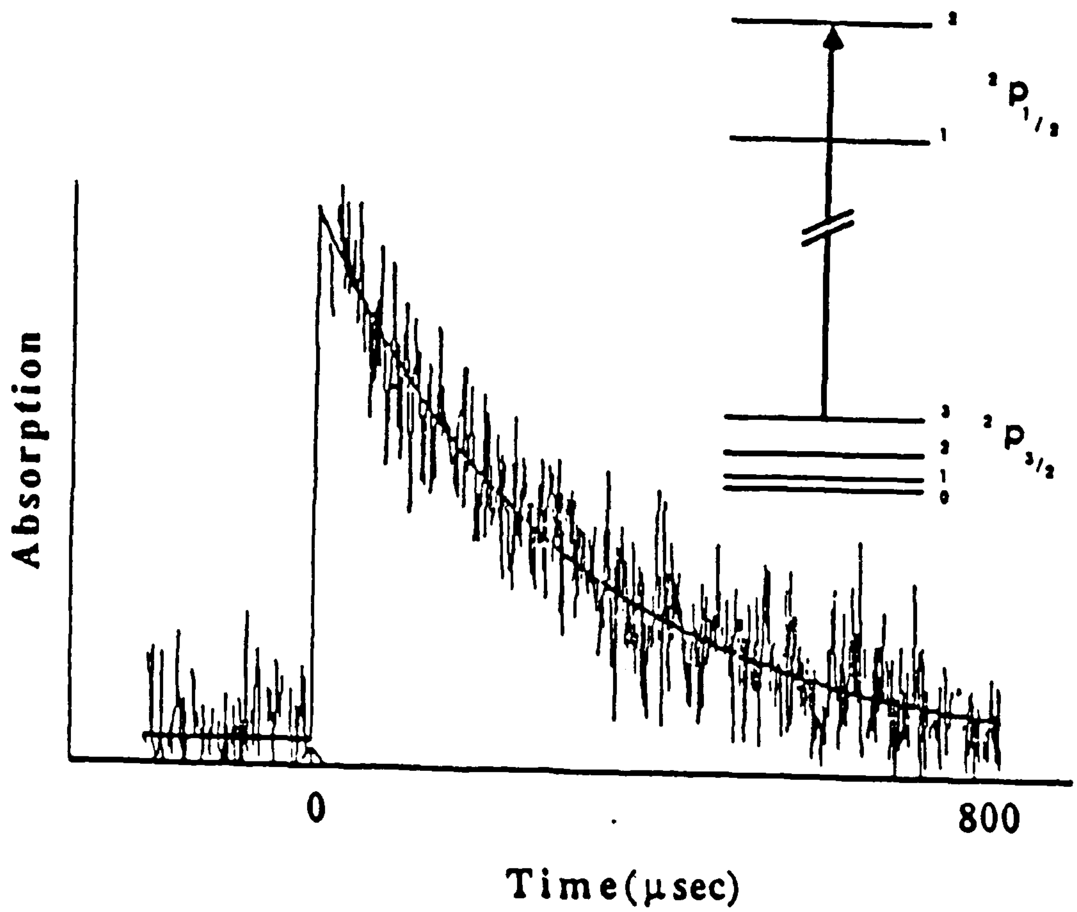

Figure 1. Chlorine atom absorption signal as a function of time. Inset shows an energy level diagram of the spin-orbit transition.

probe volume. At later times, the absorption signal decays due to diffusion of the atoms out of the probe volume. Work is currently in progress to improve the magnitude of the absorption intensity in order to utilize this technique to probe chlorine atom reactions, including recombination processes.

b. Probing Reaction Products--In addition to monitoring photo-produced chlorine atoms, we have also been successful in applying the infrared diode laser absorption technique to the study of chlorine atom reaction products. The prototype reaction which we have studied is the abstraction of deuterium atoms from D_2S.

$$Cl + D_2S \rightarrow DCl + DS \tag{3}$$

There are three DCl nascent vibrational states, v=0,1,2, which are energetically possible from this reaction. It is known that the v=1 state is initially more populated than is v=0, making the reaction a source for a chemical laser.[4] The relative populations produced in the v=1 and v=2 states have been probed by infrared chemiluminescence studies.[5] This technique does not allow the relative v=0 population to be determined. By use of time-resolved infrared absorption to probe the DCl product, we have been able to determine, for the first time, the relative v=0 population produced in this reaction. This is important for the evaluation and development of statistical models for energy distribution in the products of chemical reactions. In addition, we have been able to determine the rate of this reaction. The ultimate goal of these experiments is to be able to determine the rotational and translational energy distributions of reaction products, taking full advantage of the extraordinary power of the diode laser absorption technique.

The basic experimental approach for the study of chemical reactions is similar to that used for the direct detection of chlorine atoms. One important change is the substitution of S_2Cl_2 for Cl_2 as the source of chlorine atoms. This serves to eliminate secondary radical chain reactions which may also produce the species being probed, DCl. The change in the diode laser absorption due to DCl molecules with a particular vibrational, v, and rotational, J, quantum number is monitored as a function of time:

$$S_2Cl_2 + h\nu(340\ \text{nm}) \rightarrow Cl + \text{other products} \tag{4}$$

$$Cl + D_2S \rightarrow DCl\ (v=0,1,2;\ J) + DS \tag{5}$$

$$DCl\ (v;\ J) + h\nu\ (\sim 4.6\ \mu m) \rightarrow DCl\ (v+1;\ J\pm 1) \tag{6}$$

Figure 2 shows a typical signal obtained when a transition from some particular rotational level of the v=1 state is monitored. The rate of the initial increase in absorption is due to the rate of the reaction. The decay in signal is due to collisional quenching of the molecules into the v=0 ground state. In contrast to the results presented for chlorine atom detection, the high pressures employed in these experiments preclude any significant contribution from diffusion to the decay of the signal. The time-dependent behavior of the less intense signals observed from v=2 states is similar to that shown in Figure 2.

The signals obtained when monitoring the v=0 level do not resemble those obtained for the v=1 and v=2 levels. Figure 3 demonstrates the time-dependent behavior of the v=0 level. The initial signal is negative-going, representing gain rather than absorption. This is due to the population inversion produced in the reaction. The amount of gain is proportional to the difference in populations between the v=1 and v=0 states. At later times, the population in v=0 increases as molecules relax from v=1 and v=2 states. The rate of growth of the v=0 population is the same as the rate of v=1 decay observed under the same pressure conditions. The v=2 signals decay more quickly, as would be expected. From these measurements we have determined that 32% of the molecules are initially formed in v=0, 60% are in v=1, and 8% are in v=2. The relative populations in the v=1 and v=2 states agree with the values determined by chemiluminescence techniques within the reported uncertainty limits.[5] Current work involves extending this technique to other systems, such as chlorine reacting with deuterated formaldehyde or ethane, and also determining the rotational and translational energy distributions in the reaction products.

In addition to determining the product energy distributions following a chemical reaction, these same time-resolved absorption measurements also allow the reaction rate to be obtained. The reaction should be first order in D_2S concentration due to the low concentration of chlorine atoms produced

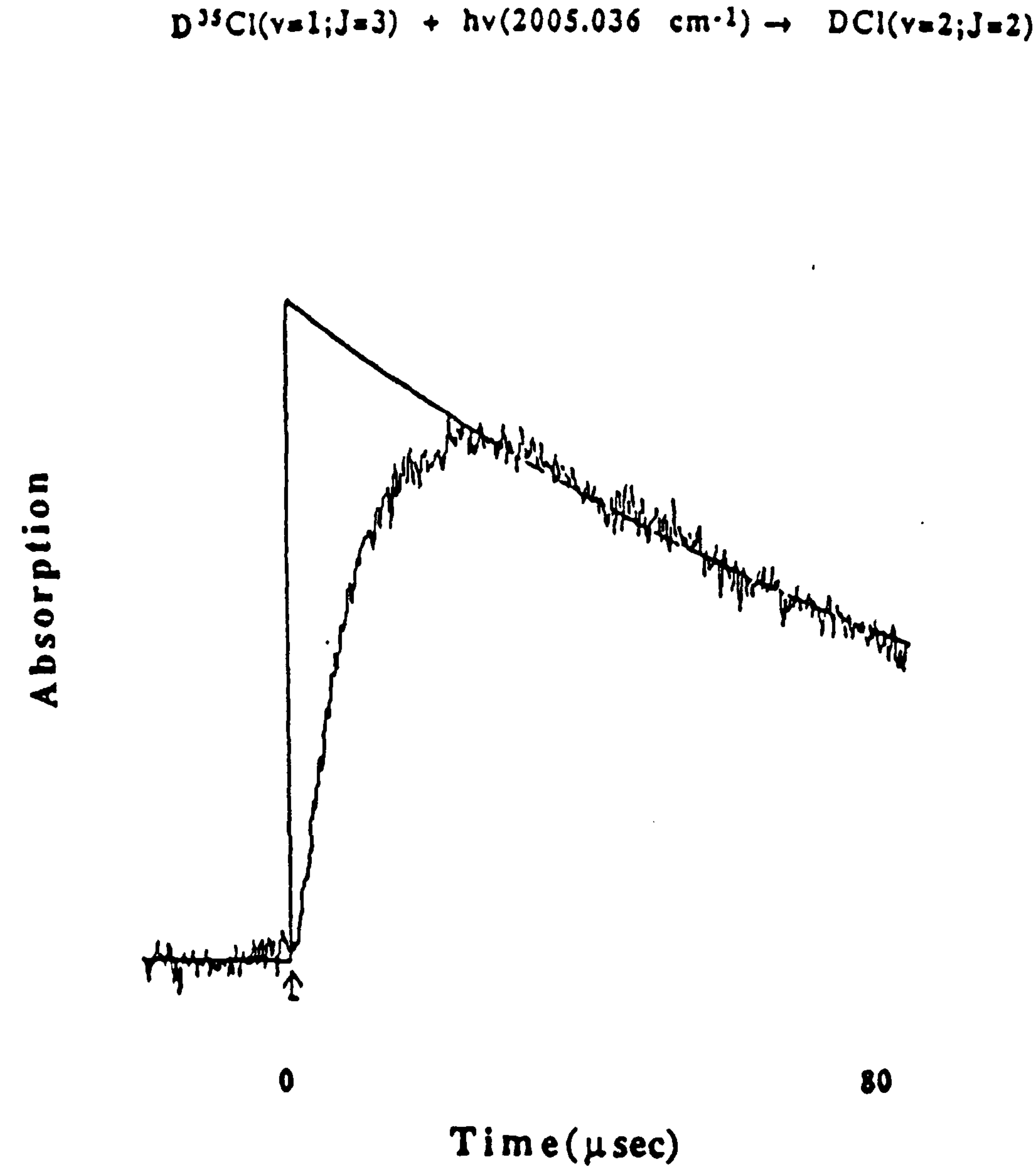

Figure 2. DCl absorption signal as a function of time.

$D^{35}Cl(v=0;J=6) + h\nu(2160.069\ cm^{-1}) \rightarrow DCl(v=1;J=7)$

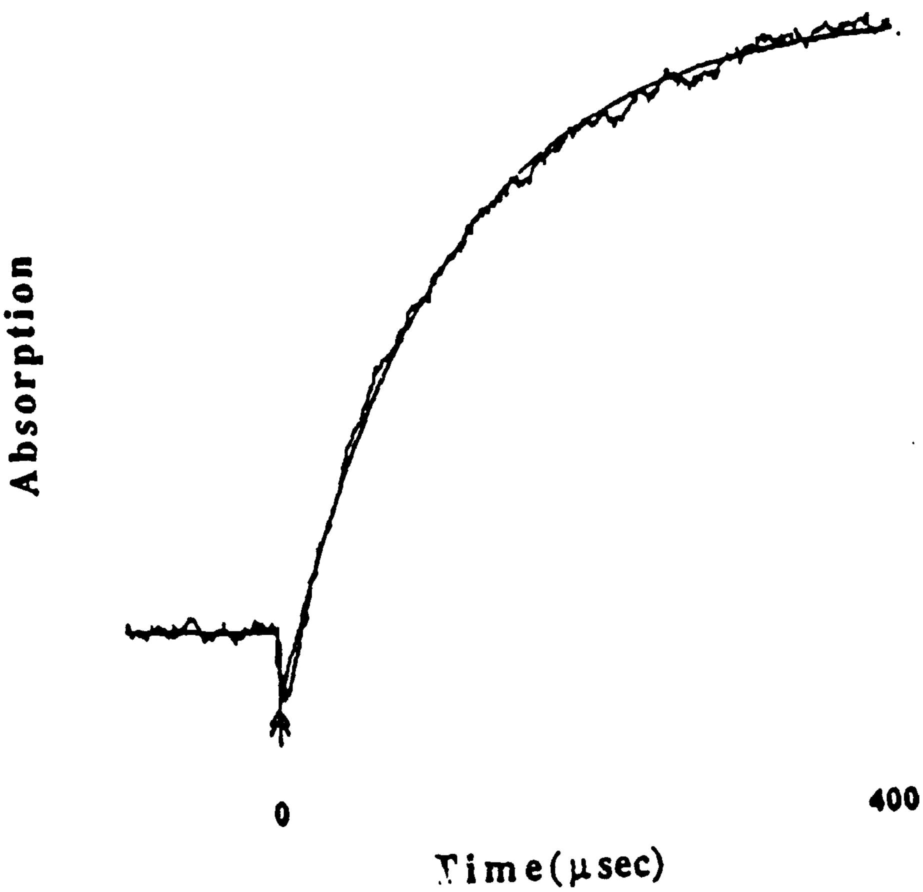

Figure 3. DCI absorption signal as a function of time.

by the photolysis pulse. By varying the D_2S concentration and measuring the rate of the initial rise in the v=1 signals, we have obtained a preliminary value of 3 x 10^{-11} cm^3 $molecule^{-1}$ sec^{-1} for the rate constant. This is in agreement with the expectation that the rate constant will be slightly lower than that obtained for the reaction of Cl with H_2S[6], 6 x 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}, due to the kinetic isotope effect.

3. <u>Summary</u>--Time-resolved infrared absorption experiments, using tunable diode lasers, can be used to probe the dynamics of chlorine atom reactions. We have been able to monitor chlorine atoms directly by probing the atomic spin-orbit transition at 11.3 μm. In addition, we have extended our experimental technique to probe the products of chemical reactions, determining the reaction rate and vibrational energy distributions. Future experiments will involve applying the chlorine probe technique to reactive systems and determining the rotational and translational energy distributions of reaction products.

This research was also supported by the National Science Foundation, Grant CHE-85-1746, the Office of Naval Research, Contract N00014-86-K-0694, and the IBM Materials Research Award.

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C. ROTATIONALLY RESOLVED EXCITATION OF $CO_2(01^11)$ BY COLLISIONS WITH HOT HYDROGEN ATOMS

(F. A. Khan, T. G. Kreutz, J. A. O'Neill, C-X Wang and G. W. Flynn, Columbia University; and, R. W. Weston, Jr., Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973)

1. Introduction--State resolved experimental information pertaining to energy transfer into ro-vibrational degrees of freedom of small molecules is of considerable interest, both per se, and because of the usefulness of such data in testing potential surfaces which provide a direct detailed picture of the dynamics of unimolecular and bimolecular reactions. The simplest of collisional encounters is one between a translationally "hot" (fast moving) atom and a small molecule, leading either to a chemical reaction or to vibrationally-rotationally inelastic scattering. State-resolved experiments involving translationally "hot" hydrogen atoms (referred to as H* in this report) have provided a great deal of information about these types of collisional encounters. The subject of reactive and non-reactive "hot" atom collisions has been reviewed recently.[1]

The system $H^* + CO_2$ has been well studied both experimentally and theoretically. Wolfrum and co-workers[2] have observed reactive collisions:

$$H^* + CO_2 \rightarrow OH + CO \qquad (1)$$

The influence of reactant orientation on product state distribution has been determined by Wittig and co-workers[3] who studied the corresponding van der Waals reaction:

$$HBr.CO_2 \rightarrow OH + CO + Br \qquad (2)$$

Recently, Zewail, Bernstein and co-workers[4] have studied the van der Waals reaction:

$$HI.CO_2 \rightarrow OH + CO + I, \qquad (3)$$

observing for the first time the real (picosecond) time birth of OH. An ambitious study of the H + CO_2 system by Schatz[5] and co-workers, using a quasi-classical trajectory approach with a "full" potential surface to calculate distributions of final states, predicts the reactive data very well. However, an extremely sensitive test for the potential surface used and the theoretical techniques employed in studying this system is provided by vibrationally-rotationally inelastic scattering data. The aforementioned calculations by Schatz and co-workers indicate that the ν_3 (anti-symmetric stretch) vibration in CO_2 is excited largely by end-on collisions with H atoms, while broadside collisions are more significant for exciting ν_2 (bend) vibrations. Previous work has shown that while the 00^01 distribution[6] peaks at J = 31, the 01^10 distribution[9] peaks at J = 43, a significantly different result, which can be attributed to the effect of different trajectories on the efficiency of collisional excitation for different vibrational states. An interesting comparison is now possible between theory and experiment, since the 01^11 state is a combination bend-stretch state. An interesting property of states of CO_2 with non-zero vibrational angular momentum predicted theoretically by Alexander and Clary[7,8] for low energy He/CO_2 scattering is alternation in the intensity of odd and even J states. This is at least in part due to the symmetry properties of the 3J symbols which enter the scattering amplitudes for even and odd states. Indeed, the first observation of such a propensity in CO_2 was for the H/CO_2 system with E = 2.3 eV for the 01^10 state[9] wherein the odd J states were populated more heavily than the even J states. Because of a change in the vibrational wave-function in the 01^10 state compared to the 01^11 state, the reverse propensity (even J states more heavily populated than the odd J states) is expected for 01^11. Preliminary data[9] indeed showed this to be the case. We report here in detail the rotational distributions for both the even and the odd rotational states of CO_2 (01^11) produced by collisions with 2.3 eV hydrogen atoms.

2. Results and Discussion--The double resonance excimer laser photolysis and diode laser probe apparatus used in our experiments has been described elsewhere.[6, 10] Processes investigated in the present study can be summarized as follows:

H_2S + hv (193 nm) $\rightarrow$ H* + HS (Photolysis of H_2S)

H* + CO_2 $\rightarrow$ H + CO_2 (01^11;J) (Excitation of CO_2)

CO_2 (01^11,J) + hv (4.3 μm) $\rightarrow$ CO_2 (01^12;J+1). (Diode laser probe) (4)

The vibrational states of CO_2 are designated (mn^lp) ,where m, n, p are respectively the number of quanta of symmetric stretching, bending and asymmetric stretching motions of CO_2.

While determining the rotational distribution[6] for CO_2 (00^01) following collisions with hot hydrogen atoms, great care was excercised to ensure that the rotational distribution determined for sample pressures of 15-50 mtorr was largely a result of a single collision of H atoms with CO_2 molecules. A complete treatment of rotational relaxation of ro-vibrationally excited CO_2 molecules and the diffusion of H atoms from the probe beam was developed. The results obtained here under nearly identical conditions can also be ascribed to a single H*/CO_2 collision.

Preliminary data[8] obtained in this laboratory showed that there is a propensity for even 01^11 rotational states to be populated over the odd rotational states, hence rotational population distributions were determined for even and odd rotational states by monitoring the following transitions in CO_2.

$01^11 \rightarrow 01^12$ R (6, 14, 20, 22, 24, 28, 30, 32, 34, 40, 48, 52, 56, 60)

$01^11 \rightarrow 01^12$ R (5, 11, 15, 17, 19, 25, 27, 31, 35, 41, 47, 51) (5)

The populations of rotational levels within the 01^11 states are best determined by fitting parts of the absorption signals between 1 and 15 μs with growing and decaying exponentials. All processes corresponding to collisional relaxation are then extrapolated to time t = 0 and subtracted from the total signal in order to obtain the signal amplitude corresponding to the "instantaneous" H*/CO_2 excitation process. The higher the sample pressure, the faster the filling process for low lying rotational states due to rotational relaxation of the high rotational states; hence, the experiment is

best performed at pressures as low as possible. Poor signal to noise quality at very low pressures limits the accuracy of computer fitting of the data, hence the experiments were performed at sample pressures of 35 mtorr, where signal quality is quite good and rotational relaxation relatively slow. (At this pressure, 3.3 μs are required for a collision of an excited CO_2 molecule with either CO_2 or H_2S, a time corresponding to nearly 4.5 times the response time of the detection system.)

The amplitudes corresponding to the direct population of different rotational levels by collisions with H* were determined as described above. These amplitudes, when normalized by appropriate diode laser power, yield the relative populations of the rotational levels in the 01^11 vibrational state produced by H* collisions. These are plotted in Figure 1. Two features are immediately obvious from this plot:

(1) The population in a given even rotational state is higher than that in the adjacent odd rotational state.

(2) The rotational distribution for the even states peaks at J = 34, while that for the odd states peaks at J = 35.

The technique of time-resolved sub-Doppler spectroscopy was recently developed and applied to probe the transient linewidths[11] of CO_2 after interaction with H*. We report here another method for measuring transient linewidths. Briefly, the transient signal is input into a boxcar integrator with 10 ns wide gates fixed at 0 ns (defined by the excimer pulse) and 700 ns (the response time of the detection system). Simultaneously, the IR light passing through the reference cell is chopped at 50 Hz, and the chopper triggers a lock-in amplifier (time constant 10 s). With a confocal etalon placed after the reference cell, and the modulation of the diode laser turned off, the line in question is slowly swept by fixing the temperature and scanning the current of the diode laser. The dc output of the difference of the boxcar gates is now seen as the transient linewidth on a signal averager (Lecroy 9400) while the dc output of the lock-in amplifier is the etalon trace, providing a simultaneous calibration. Both the signal and the etalon calibration are well fit by gaussian functions and yield linewidths in excellent agreement with those obtained by the first

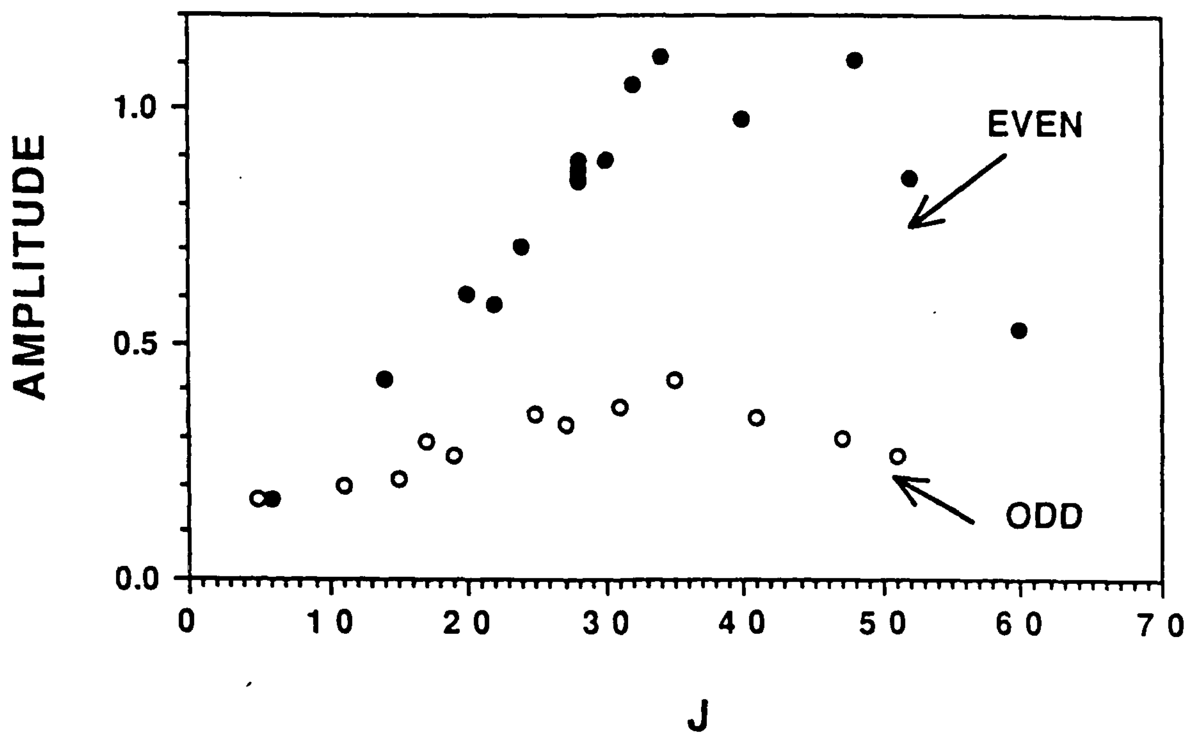

Figure 1. Shown is the measured, rotationally resolved inelastic scattering into CO_2 (01^11) at 298 K. The scattering into the even rotational levels is substantially larger than into the odd rotational levels. Transient linewidths, which are substantially larger than the room temperature Doppler values, have been taken into account.

technique.[11] Linewidths obtained for the 01^11 state are shown in Figure 2. The linewidths for even rotational states are larger than those for the odd rotational states; in each case they increase with increasing J.

At room temperature, 8% of the CO_2 molecules are in the 01^10 state, and can significantly contribute to the population of the 01^11 state by a one quantum collision induced transition, whereas a simultaneous change of two quanta is required for the ground state to populate 01^11 in a collision. Are these contributions different for the even and odd states? The difference in transient populations and transient linewidths that we report here at room temperature makes this an interesting possibility. A simple test of this hypothesis is to shrink the population of 01^10 by lowering the sample temperature, and to determine the population in 01^11. Such experiments are underway.[12]

This research was also supported by the Department of Energy, Contract DE-FG02-88-ER-13937, the National Science Foundation, Grant CHE-85-17460, and the IBM Materials Research Award.

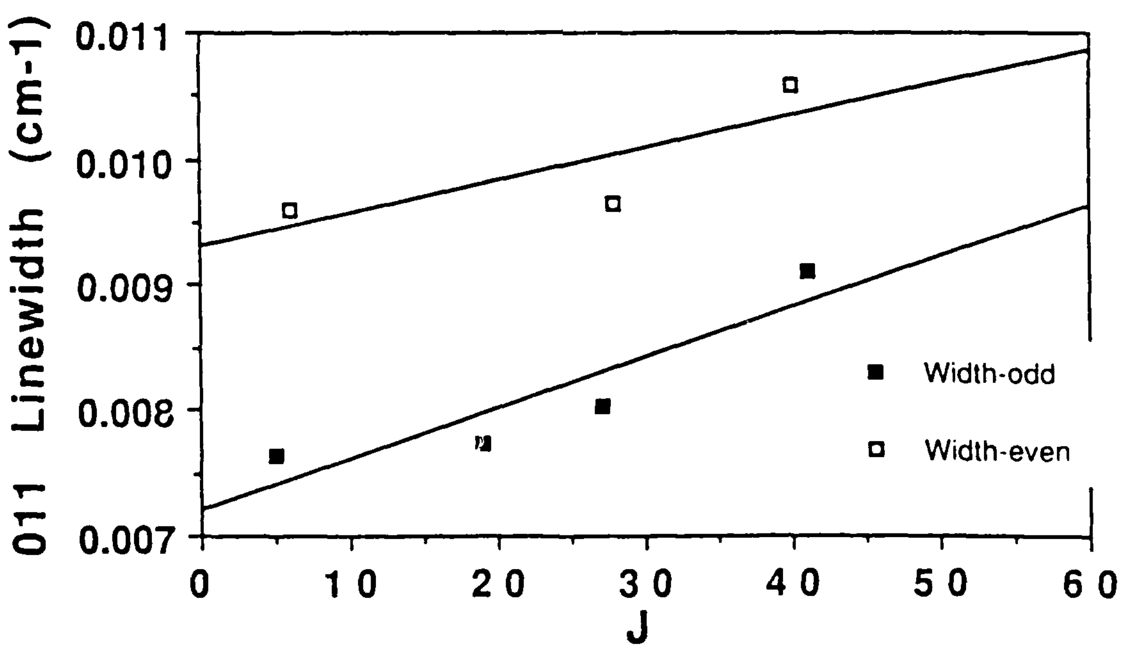

Figure 2. The transient linewidths for CO_2 (01^11) are shown. The linewidths for the even rotational states are noticeably larger than those for the odd rotational states; in either case they increase with increasing J. The solid lines are the best fit straight lines.

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12 Work in progress.

SIGNIFICANT ACCOMPLISHMENTS

A CW focused UV laser has been used to do photoemissive mapping of a semiconductor surface. This technique provides a simple non-invasive way to plot doping patterns on the semiconductor surface.

Recent studies on Pt/Ti/GaAs and Ti/Pt/GaAs diodes proved that the bimetal Schottky structure provides a new and useful approach to study the fundamentals of metal-semiconductor interfaces. Using this approach we found that the metal screening lengths for Pt and Ti are 6.5Å and 7Å, significantly greater than the usual estimates in the Mott-Jones theory. This discovery indicates that the interfacial potential drop inside the metal plays an important role in the Schottky barrier formation. This method also provides the information about the density of state distribution at the metal-semiconductor interface. Control of the barrier height through the tailoring of the intermediate metal thickness and compositions may be useful in device applications.

Experimental methods for performing high pressure measurements in diamond anvil cells were developed and used at Columbia for the first time. These techniques require careful development and have been employed successfully in relatively few laboratories. Experimental apparatus for photoluminescence and modulation reflectance spectroscopics were also assembled and used to analyze semiconductors. The first spectroscopic study of II-VI semiconductors was also performed. This photoluminescence measurement of a ZnSe epilayer on a thinned GaAs substrate was performed at 10K, and exhibited the narrow excitonic features needed for the upcoming study of II-VI superlattices at high pressure and low temperature.

New effects in the phenomena of sum- and difference-frequency beats in time-delayed four-wave mixing experiments have been discovered and studied. The peaks in the modulation pattern as a function of time delay have been observed to narrow in higher diffraction order signals, and our theoretical analysis predicts similar behavior in the large pulse area (or intense field) limit.

Silent (photon-number-squeezed) light has been generated as recombination radiation from semiconductor materials by using a specially designed space-charge-limited light-emitting structure.

Calculations have shown that the mean number of photons required per bit for a lightwave communication system can be reduced significantly by the use of silent light.

The open-loop fully quantum theory of light detection has been extended to include closed-loop operation; the unmistakable signatures of nonclassical light associated with open-loop detection do not carry over to closed-loop systems.

An extremely efficient energy transfer process has been discovered in which the electronically excited ion pair (D) state of I_2 collisionally pumps vibrational levels of small molecules.

Infrared diode lasers have been used for the first time to follow chemical reactions in quantum state resolved detail. The first quantitative measure of the v=1/v=0 population inversion in DCl formed by the reaction of D_2S and Cl has been made.

Velocity recoils due to high energy collisions have been measured using infrared diode lasers. The variation in recoil velocity with final quantum state provides a wealth of information about collisions and energy transfer processes which are of importance in gas laser development.

TECHNOLOGY TRANSITIONS

A large system for studying laser processing of silicon has been established within IBM. Several of the features in this system were transferred directly from work on laser etching at Columbia in Professor Osgood's laboratory.

Professor Hartmann's work on photon echoes has been used in conjunction with samples provided from the ARO-VRI center at Michigan to measure for the first time, coherence relaxation times in heterostructures.

Through his joint work with Professor Teich, Federico Capasso of AT&T Bell Laboratories has carried out a study of space-charge-limited mechanisms involved in the generation of recombination radiation with the properties of silent light.

Because earth-based and space optical communications are adversely affected by the presence of cosmic rays, Dr. Rudy Buser of the Army Night Vision Laboratory has expressed interest in Professor Teich's studies of the effect of cosmic-ray noise in optical systems. Professor Teich and his students have carried out measurements and developed a theory for the optical noise introduced by such processes.

A collaboration between Columbia and Professor R. Gunshor's group at Purdue University started this year as a result of the JSEP work unit. Professor Gunshor is supplying (and has supplied) us with MBE-grown II-VI semiconductors. He is supported by ONR, AFOSR and NSF.

A patent application on controlling the Schottky barrier height using an interfacial thin metal film is being finished through the Department of Science and Technology, Columbia University.

Scientists at IBM Almaden and Fishkill laboratories have begun to consider the use of infrared diode laser techniques, developed in Professor Flynn's laboratory, to study gas/surface chemical reactions and photo-ablation phenomena.

PERSONNEL

Faculty

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